Long-term Tannery Waste Contamination: Effect on Chromium Chemistry

Thesis submitted for the degree of
Doctor of Philosophy
at
The University of Adelaide
Faculty of Agricultural and Natural Resource Sciences

by
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2002

CORRIGENDA

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Chapter 8		
Page 165, lines 2,4, 5,7,10 and 11:	leachate	pore water
Page 166, lines 1, 3, 6, 8, 11 and 13:	leachate	pore water
Page 167, lines 2, 3, 7, 11 and 12:	leachate	pore water
Page 169, lines 3 and 21:	leachate	pore water
Chapter 10		
Page 203, lines 3,12,17,19, 20 and 21:	leachate	pore water

References added

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Abstract

Of all the agricultural industries the leather industry appears to be the major source of pollution in many countries throughout the world. While the primary production phase of the industry (e.g. animal production) has only minimal environmental impact, the value-adding phase (tanning and processing) has a broad-scale impact. From data supplied by Australian and Indian scientists, and from direct observation of crop growth in affected agricultural areas, it is evident that borehole water beneath large areas is becoming salinised. Furthermore, soils surrounding tanneries are being polluted through the disposal of chromium-rich effluents to agricultural land. The ability of soils at these contaminated sites to sorb Cr is highly variable and appreciable amounts of Cr have been recorded in the subsurface soils. The potential risk of surface and ground water contamination by Cr at these sites is a major environmental concern. Factors that influence adsorption capacity of soils influence the bioavailability and subsequent mobility of Cr in soils. In the present study we investigated the factors that influence mobilization and migration of Cr in surface and subsurface soils from a long-term tannery waste contaminated site, at Mount Barker, Adelaide, South Australia.

In particular, the study focused on the effect of long-term contamination (a) on the solid phase speciation of chromium (Cr), (b) the solution (pore water) composition of tannery waste contaminated soils on mobility of Cr and (c) the potential options for remediation of Cr contamination in the soils from surface (0 - 15 cm) and subsurface (> 50 cm) layers. Together with these studies, this thesis also examined the possible remediation of hexavalent Cr, Cr(VI), from wastewater using Lanthanum salts (La^{3+}). These studies were under-pinned by a preliminary study that assessed the exiting

techniques for speciating solution phase Cr (III) and Cr(VI) using capillary zone electrophoresis (CZE).

A simple method was developed for the simultaneous determination of Cr(III) and Cr(VI) by capillary zone electrophoresis (CZE), where Cr (III) was chelated with ligands to form anionic complexes. Of all the ligands studied, the 2,6-pyridinedicarboxylic acid (2,6-PDCA) complex with Cr (III) gave the largest UV response and highest selectivity for Cr (III). In addition, the condition for pre-column derivatization, including pH, concentration ratio [Cr (III)/ 2,6-PDCA] and the stability of Cr (III) complexes were also examined. Although the new method showed excellent separation of Cr(III) and Cr(VI), its sensitivity at low levels of detection (< 10 μg/L) Cr(VI) was poor compared to conventional ion chromatography (IC). For this reason, all aqueous phase speciation was conducted by using IC.

Solid phase speciation of the soils from surface and subsurface layers showed varied partition status for Cr in different soil fractions. The total Cr concentration exceeded 9% in the surface horizon and 0.05% in the subsurface horizon. Sequential fractionation studies revealed that more than 91% of total Cr is bound with the H_2O_2 extractable organic fraction in soil from the surface layer while only 45.3 % of total Cr was bound to the H_2O_2 extractable organic fraction in the subsurface soil. The other major portion of Cr was bound to the residual fraction (42.2%) in soil from the subsurface layer. The dominance of organic bound Cr was not surprising given the presence of a high proportion of organic carbon in the surface soil (10 %) compared to soil from the subsurface layer (<3 %). The association of Cr with organic matter was further confirmed by solid state ^{13}C CP/ MAS NMR study. These studies reveal T_1H relaxation rates typifying metal-organic matter binding. Indeed, when Cr was treated with collagen, the resulting relaxation rate was similar to that obtained for the tannery waste contaminated soil indicating the predominance of protein structures of the organic wastes present in the contaminated site.

Chromium bound to the water-soluble and exchangeable fraction (phosphate exchangeable) although low in both surface and subsurface soils, exceeded both Australian and USEPA permissible levels. This suggested that a significant concentration of Cr was bioavailable in these contaminated soils. Indeed, sequential desorption studies revealed slow but continuous release of Cr in water extracts of the surface soil illustrating the potential for slow but continued loading of subsurface layer with Cr. Desorption of Cr was further enhanced in the presence of P at concentrations exceeding 1.6 mmol/L. Since both chromate and phosphate are adsorbed by similar specific adsorption mechanisms it is not surprising to see enhanced release of Cr(VI) by phosphate. Aqueous speciation of Cr showed that Cr(VI) was the predominant species released in water and phosphate exchangeable fractions in soil from the surface layer and only Cr(III) was released in the strongly acidic soil from the subsurface layer.

The presence of high concentrations of water extractable and exchangeable Cr in the contaminated soils necessitated the investigation of the effect of tannery waste dominant electrolytes, Ca^{2+}, Na^{+}, Cl^{-} and PO_4^{3-} on Cr desorption in the contaminated soils. These studies revealed contrasting results for desorption of Cr in soil from surface and subsurface layers. This was attributed to the markedly different forms of Cr in the alkaline surface (Cr(VI)) and subsurface acidic soil (Cr(III)). Both batch and column leaching studies showed similar trends in the desorption behaviour of Cr for the soils from the contaminated site. In the alkaline surface soil, Cr release decreased with increasing cationic charge (water $\geq Na^{+} > Ca^{2+}$) while the trend was reversed ($Ca^{2+} > Na^{+}$ > water) in the acidic soil from subsurface layer.

In the alkaline surface soil the presence of Ca^{2+} in the system favoured greater retention and less mobility of Cr(VI) compared to Na^{+}. Detailed investigations using these soils suggest that the enhanced binding of Cr(VI) in the presence of Ca^{2+} may be attributed either to the electrolyte effect on the diffuse double layer together with the pH of the system or due to the presence of high concentrations (15%) of calcite (SEM study) which could lead to precipitation of $CaCrO_4$ on calcite surfaces.

The presence of Cr(VI) in water and phosphate extracts is of concern to both regulators and the public living adjacent to the contaminated site. For this reason, an attempt was made to develop strategies that minimise (a) Cr content of leachates and (b) the mobility of Cr at the contaminated sites. Lanthanum chloride salt was effective in removing Cr(VI) from solutions as a $La_2(CrO_4)_3.7H_2O$ precipitate. The formation of $La_2(CrO_4)_3.7H_2O$ precipitate was supported by the X-ray diffraction (XRD) patterns of the purified precipitates. At high initial concentrations of Cr(VI) (0.1 M), Cr(VI) removal was 98% at a 1:1 mole ratio and 93% at a 1:2 mole ratio of La^{3+} to Cr(VI). However, in practice more La^{3+} was required to remove Cr(VI) at low initial concentration of Cr(VI) (1 mM). The ratio of 5:1 of La^{3+}:Cr(VI) effectively removed 99% of Cr(VI) from solutions. In general, the pH range of 6 – 8.5 was found to be ideal for complete removal of Cr(VI) from solutions by La^{3+}.

In the soil remediation study, Fe salt was used to enhance binding of Cr(VI). Preliminary batch and incubation studies showed effective transformation of Cr(VI) to Cr(III) by reduction. Soil equilibrated and maintained at constant moisture (50% field capacity) with an optimal dose of 2.5 % Fe(II) (on soil weight basis) showed complete reduction of water soluble Cr(VI) within 14 days. In contrast, there was >80 % reduction of exchangeable Cr(VI) over the same period. However, prolonged incubations studies for 110 days with wet and dry cycles revealed the reappearance of aqueous Cr(VI) after

14 days treatment. Given that Fe(II) loading in these soils exceeds the minimum concentration needed for complete reduction of labile Cr(VI) the reappearance of Cr(VI) may suggest loss of Fe(II) either via an ion exchange process or via oxidation of Fe(II) to Fe(III)(OH) which is an insoluble compound. The rate of desorption of Cr(VI) or the solubility of Cr(VI) in this contaminated soil may also be a limiting factor for complete reduction of both water-soluble and exchangeable Cr(VI) by Fe(II). This thesis also discussed other possibilities for the reappearance of Cr(VI) including possible chemical oxidation by MnO_2.

Cr(VI) stabilization studies in a 30 cm intact core also showed a decrease in the concentrations of aqueous Cr(VI) when Fe(II) was applied to the surface 5 cm. This equated to nearly 95% reduction of aqueous Cr(VI) in the Fe(II) treated zone compared to the untreated zone. However, the concentration of aqueous Cr(VI) again increased from day seven despite the mixing of an excess Fe(II) (3 % on soil weight basis) to a depth of 4.5 cm in the intact core. The reasons for the lack of complete reduction and reappearance of Cr(VI) may be due to the presence of a large pool of labile Cr(VI) and the limiting amount of added Fe(II). This limitation in Fe(II) may be due to (a) leaching of Fe(II) to subsurface soils (but no Fe was detected in the pore water ~~leachates~~ from subsurface ports), (b) the loss of Fe(II) due to ion exchange processes and oxidation to Fe(III)(OH).

The effluent collected from the 10-30 cm zone showed higher concentrations of Cr compared to the concentration of Cr released into the 5 cm port pore water ~~leachate~~ and this was even greater than that recorded for the untreated zone at a depth of 10 cm. Speciation studies showed that Cr in the effluent was predominantly Cr(VI). This suggested that Fe(II) incorporated into the surface layer was not effective in reducing soluble Cr(VI) in the 10 - 30 cm layer.

Statement

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university or tertiary institution. To the best of the author's knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

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Acknowledgments

I would like to express my gratitude to my principal supervisor Dr. Ravi Naidu for his excellent advice, interesting ideas, generosity and constant encouragement over the period of my study.

I would also like to thank my co-supervisors Drs. Rai Kookana, Angus Alston, and David Chittleborough for their excellent advice, constructive criticism and support during the period of my study.

I express my heartfelt thanks to Professor Ramasamy for creating the opportunity to do research abroad.

I owe much to number of people for the existence of this thesis. I express my heartfelt thanks to Lester Smith for sharing his enormous experience in metal analysis, laboratory skills and technical advice through out the period of my stay in Adelaide. My heartfelt thanks goes to Damian Mowat for all his help from the day he received me at CSIRO until the day of my departure from Adelaide.

I express my gratefulness to Euan Smith and Julie Smith for their help, hours of discussions and useful ideas during the course of my study.

My special thanks goes to Megharaj for introducing me to microbial studies and for all help, technical and personal during the entire period of study and until submission of the thesis.

I am very much grateful to many visiting scientists to CSIRO for their inputs in to this thesis, notably, to Dr. Krishnamurthi for solid phase speciation studies and Drs. Walter Wenzel and William Inskeep. I would also like to express my heartfelt thanks to Professor. Sethunathan for sharing his lifetime experience as a great academician. I gratefully acknowledge Dr. Rengasamy for his useful discussions on wide range of topics during the entire course of study period.

I am also very much grateful to Ron Smernik for running samples in NMR and interpretation of the results. I gratefully acknowledge Chen Zuliang for his help in CZE work and interpretation of the results.

I profusely thank Adrian and his team for their help in using Ion Chromatography for Cr(VI) analysis and Bernie for lanthanum analysis in ICP. I appreciate all the help extended to me by staff members from CSIRO Land and Water and Department of Soil and Water.

I express my heartfelt thanks to one and all who had stayed with me in "mushroom" office during the study and special thanks to Sara Parwin and Gary Owens for their help and useful discussions throughout the entire period and until submission of the thesis.

I would also thank my fellow students, especially Ajit Sarmah and Riaz Ahmed, for their help and encouragement during this work. I express my thanks to John Davy, Ms. Niranjala and Ms. Sandra for their administrative support during the study time.

I am very much grateful to the University of Adelaide and ACIAR for providing the opportunity and scholarship support for this study. I would also like to gratefully acknowledge Tamil Nadu Agricultural University for the grant of study leave to do this work.

I express my gratitude to my parents, in-laws and friends for their patience and continued support during the entire course of my study.

Finally, my heartfelt thanks to my wife ***Saroja*** and daughter ***Maanasa*** for their long patience, encouragement and moral support throughout the study period.

"Good on you", to all who have helped in this accomplishment.

Dedication

I would like to dedicate this thesis to
my father S.V. Subramanian for his inspiration

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CHAPTER 1

General Introduction

Soil contamination by heavy metals is extremely deleterious to ecosystem (ie. environmental and human) health because these contaminants are environmentally persistent. Unlike most organic contaminants, heavy metals are generally refractory and cannot be degraded or readily detoxified biologically. Chromium (Cr) is one of the most commonly found heavy metal contaminants in soils of industrialized nations (Ellis et al., 1984).

Commercially, Cr compounds are commonly used directly in leather tanning and for electroplating, and as additives in the production of pigments, catalysts, corrosion inhibitors, and wood preservatives. Chromium metal is also widely used in steel industries through out the world. However, in terms of wide spread Cr contamination of soil, the use of Cr ore processing residue (COPR) as the construction or landfill material in several countries, including England, Japan, West Germany, and the United States is the most extensive (McKee, 1988). After COPR, Cr contamination of sites via the indiscriminate disposal of tanning industries liquid and solid waste into soil and surface water bodies is the most prevalent. Soil and groundwater contamination of Cr through dumping of tannery waste is commonly observed in developing countries, especially South East Asian countries (Naidu et al., 2000a). Chromium has attained wide public and regulatory attention because of its toxicity to environmental ecosystems under a certain oxidation state.

Chromium exists in highly variable oxidation states from +2 to +6 and is also known to form both anionic and cationic complexes, examples include $Cr(OH)^{2+}$, $CrO_4^{2-}$and CrO_3^{3-}. Naturally occurring Cr compounds have two principal valences, Cr(III) (chromic) and Cr(VI) (chromate), with the highly oxidized forms of Cr (Cr(VI)) being much less stable than Cr(III). The toxicity of Cr compounds to plant, animal and human has been largely associated with the Cr(VI) form, whereas Cr(III) is virtually inactive *in vivo* (Cohen and Costa, 2000). The carcinogenicity of Cr in experimental animals is well documented (see for example reviews in IARC, 1980, 1990; Cohen et al., 1993; Costa, 1997; Cohen and Costa, 1997). The toxicity and carcinogenicity of Cr species prompted extensive studies on the behavior of Cr in various environmental matrices.

Numerous investigators (Bartlett and Kimble, 1976a & b, Bartlett and James, 1988, Cary et al., 1977b, Bloomfield and Pruden, 1980, Grove and Ellis, 1980, James, 1996) have conducted extensive studies on the fate and behavior of Cr in the terrestrial environment. These studies reveal that most of the Cr in soil occurs as Cr(III) and is within the mineral structures or forms mixed Cr(III) and Fe^{3+} oxides. Since Cr(III) is slightly mobile in very acidic media and at pH 5.5 is almost completely precipitated, its compounds are considered to be very stable in soils. On the other hand, Cr(VI) (CrO_4^{2-} and $HCrO_4^{-}$) is extremely unstable in soils and is easily mobilized in both acid and alkaline soils.

Soil pH and redox potential govern Cr behavior in soils. Under the same redox potential of 500 mV, Cr(III) predominated at pH 5, $Cr(OH)_3$ was formed between pH 5 and 7 and CrO_4^{2-} occurred at pH >7. Adsorption of Cr by clays was also highly pH dependent, and while Cr(VI) adsorption decreased as pH increased, the adsorption of Cr(III) increased as pH increased (Griffin et al., 1977). Organic complexes of Cr may modify the behavior of Cr in soils however; the dominant effect of organic matter is the stimulation of the reduction of Cr(VI) to Cr(III) (Wittbrodt and Palmer, 1996b). The ready conversion of soluble Cr(VI) to soluble or insoluble Cr(III) under normal soil conditions is of great importance because it is responsible for low Cr bioavailability. However, the potential for Cr(III) oxidation in soils in the presence of Mn(IV) compounds is of concern as this process can transform relatively non toxic Cr(III) to toxic Cr(VI) (Bartlett and James, 1979). James (1996) described the Cr(III)/Cr(VI) balance as a seesaw with Mn and organic matter, where the soil pH acts as a controllable master variable that helps to set the oxidizing reactivity of Mn oxides and the reducing properties of organic matter or other compounds. These chemical reactions control the fate of Cr in the soil environment. However, most of these studies have been conducted using soils from uncontaminated environments. These soils when contaminated with Cr in the laboratory do not replicate the effect of aging on Cr bioavailability. Moreover, the seasonal fluctuations in environmental conditions, including rainfall and temperature, are often not replicated in laboratory studies. It is now well recognized that aging leads to a marked increase in the ability of soils to bind contaminants, such that a long-term contaminated soil may show major differences in contaminant bioavailability and mobility compared to freshly contaminated soils. Moreover, Cr contaminated soil environments; especially those associated with industrial wastes, pose different problems given the input of various other inorganic and organic chemicals along with Cr. This is particularly true for tannery waste contaminated sites that along with high Cr also contains high levels of other soluble salts and organic compounds.

Although the composition of tannery waste water and sludge varies from country to country, an estimate from India reports that, waste water contains high total dissolved solids, chlorides, and sulphates (Ramasamy and Naidu, 2000). Dreiss, (1986) reported that last stage sludge contains high Cr concentrations along with high concentrations of organic carbon, total N, Ca^{2+}, Mg^{2+} and Na^{+}. The chemical dynamics of Cr in normal soils are well known. However, only very few reports are available which study the influence of high concentrations of organic carbon, Ca^{2+}, Na^{+} and Mg^{2+} on the chemical behavior of Cr in a contaminated soil environment.

The release behavior of Cr(VI) from COPR enriched surface soil was reported by James (1994) and Weng et al., (1994). Using long-term tannery waste contaminated surface and sub-surface soil, Naidu and his co-researchers (Naidu et al., 2000a and Kookana et al., 2000) have studied the desorption behavior of Cr. These investigators reported significant leaching of Cr(VI) from the surface and sub-surface of contaminated soils. This study was further extended by Avudainayagam et al., (2001) who investigated the soil and solution factors that controlled Cr desorption in these contaminated soils. They found that desorption was to a large extent related to the nature of the electrolytes present in the tannery wastes. This is one of the few studies reported in the literature on long-term contaminated soils. Given the marked effect of aging on the fate and behavior of Cr there is a need for detailed understanding of the behavior of contaminants in long-term contaminated sites. Such a study will consider the effect of aging on solid phase and solution phase Cr thereby enabling one to develop strategies for managing contaminated sites. The tannery waste contaminated site at Mount Barker, Adelaide South Australia provided a unique opportunity to investigate the behavior of Cr in a long-term contaminated soil. In particular this thesis investigated the following,

- the effect of electrolytes, namely Ca^{2+}, Na^{+} and PO_4^{3-}, the dominant cations and anion commonly found in tannery contaminated soils, on the mobility of Cr from surface and sub-surface soil;
- the effect of long-term contamination on the nature of Cr species by solid phase speciation of Cr partitioned to various soil components for the surface and subsurface soil of the contaminated site;
- the efficiency of ferrous sulphate as an *insitu* chemical reductant to irreversibly reduce Cr(VI) in the contaminated surface soil under various experimental conditions; and
- the potential use of lanthanum (La^{3+}) to completely remove Cr(VI) from water.

CHAPTER 2

Review of Literature

2.1 Introduction

Chromium is the tenth most abundant element in the earth's mantle and is used in many industrial processes such as plating, alloying, tanning of animal hides, water corrosion inhibition, textile dyes, mordants, pigments, ceramic glazes, refractory bricks, pressured-treated lumber and as the trace element responsible for the brilliant red and green colours of the ruby and emerald (Petrucci and Harwood, 1993). An elevated soil and water concentration of this potentially harmful element principally results from industrial waste or spills. Because the present study was concerned with a site where tannery waste had been disposed, this review focuses on the issues of tannery wastewater contamination of soil and water.

Chromium has attained wide public and regulatory attention because of its toxicity to environmental ecosystems (including both microbes and animals) under a certain oxidation state. It has oxidation states varying between – 2 to + 6, but only the + 3 and + 6 states are stable under most conditions found in the surface environment (Cotton and Wilkinson, 1966). These two oxidation states have different toxicity and mobility. Hexavalent chromium, Cr(VI), is a known human carcinogen (via inhalation) and is mobile, whereas trivalent chromium, Cr(III), is comparatively less toxic and relatively immobile (Yassi and Nieboer, 1988).

Tanning of leather with Cr salts (Cr(III)) was first introduced in 1858 and it continues to consume considerable quantities of Cr (Thorstensen, 1976). In fact, some of the earliest processes for chrome tanning of leather used Cr(VI) chemicals to saturate the skin and then reduce them to insoluble forms. However, the standard practice now is to use a soluble trivalent compound and a masking agent, a procedure that allows the Cr to effectively penetrate the hide (Lollar, 1980). During this process Cr(III) forms cross links between the collagen fibres and gives leather its durable finish. It is this stabilised matrix that goes on to be further processed into leather products.

The wastewater discharged from tannery industries contains heavy loads of both organic and inorganic chemicals, which are typically different from other Cr polluting industries (Reemtsma and Jekel, 1997). In the past three decades, and as a result of awareness and protection of environmental health, strict environmental regulations were enacted to prevent indiscriminate disposal of tannery waste in to soil and water bodies in the developed and developing parts of the world. However, prior to the regulations many tanning industries throughout the world would have dumped their Cr-containing solid and liquid wastes to neighboring land and water bodies. The exact number of such contaminated sites would be difficult to quantify and no published reports are available listing details of such sites throughout the world. However, an overview of tanning industries and the extent of contamination are available for South East Asian countries (Naidu et al., 2000a).

The development of analytical techniques to speciate aqueous Cr, and reports of ground water contamination of Cr(VI) in the vicinity of old tannery industries, have increased the attention of scientists towards historical sites where tannery waste had been disposed.

Although Cr(III) is the predominant species discharged in tannery solid and liquid wastes, the presence of Cr(VI) in ground water in the vicinity of old tanning industries puzzled many initially. However, it was soon realized that in natural systems, manganese oxides can oxidize Cr(III) to Cr(VI) (Bartlett and James, 1979; Nakayama et al., 1981; Amacher and Baker, 1982; Eary and Rai, 1987; Saleh et al., 1989; Johnson and Xyla, 1991; Fendorf and Zasoski, 1992).

A number of highly contaminated tannery waste disposal sites may exist throughout Australia. Extensive research was carried out to investigate the extent of Cr pollution, level of Cr contamination, speciation of Cr and mobility of Cr(VI) from surface to subsurface layers by installing field lysimeters and peizometers, and collecting intact cores for laboratory experimentation from one such tannery waste contaminated site at Mount Barker near Adelaide (Naidu et al., 2000b). The present study was carried out using the same contaminated soils but the objectives were to study the effect of soil solution factors influencing adsorption and desorption of Cr, partitioning of Cr in different soil fractions and options to remediate the contaminated site.

In this chapter, published studies on the fate and behaviour of Cr under different soil and climatic conditions are reviewed and the implications for the tannery waste contaminated site discussed.

2.2 General Chemistry of Cr

2.2.1 Position in Periodic Table

Chromium, with an atomic number of 24 and mass number of 51.9961, belongs to the first series of transition metals. The elements vanadium, manganese and molybdenum surround its position in subgroup VIB of the periodic system. Its electronic configuration is (Ar) $3d^5 4s^1$.

2.2.2 Stable Oxidation States

Chromium exists in a number of oxidation states but not all are equally stable. From the reduction potential diagram constructed by Neiboer and Jusys (1988) and thermodynamic energy considerations, that show positive values of the standard electrode potential (E^o), it is clear that the reduced form is favoured, whereas negative E^o values denote that the oxidised species is relatively more stable (Fig 2.1). Consequently it is clear from this reduction potential diagram that Cr(III) is the most stable form of Cr in solution, because considerable energy would be required to convert it to either lower or higher oxidation states. Although CrO_4^{2-} is also relatively stable, its high positive reduction potential means that it is strong oxidizing agent and unstable in acid solutions. This is especially true in the presence of electron donors, such as Fe^{2+}, H_3AsO_3, HSO_3^- and all organic molecules with oxidizable groups (alkanes, alkenes, alcohols, aldehydes, ketones, carboxylic acids, mercaptans etc.) (Wiberg, 1965; Beattie and Haight, 1972). Because Cr(III) and Cr(VI) forms are the most stable Cr species in the environment, the chemistry of these species are discussed in the following sections.

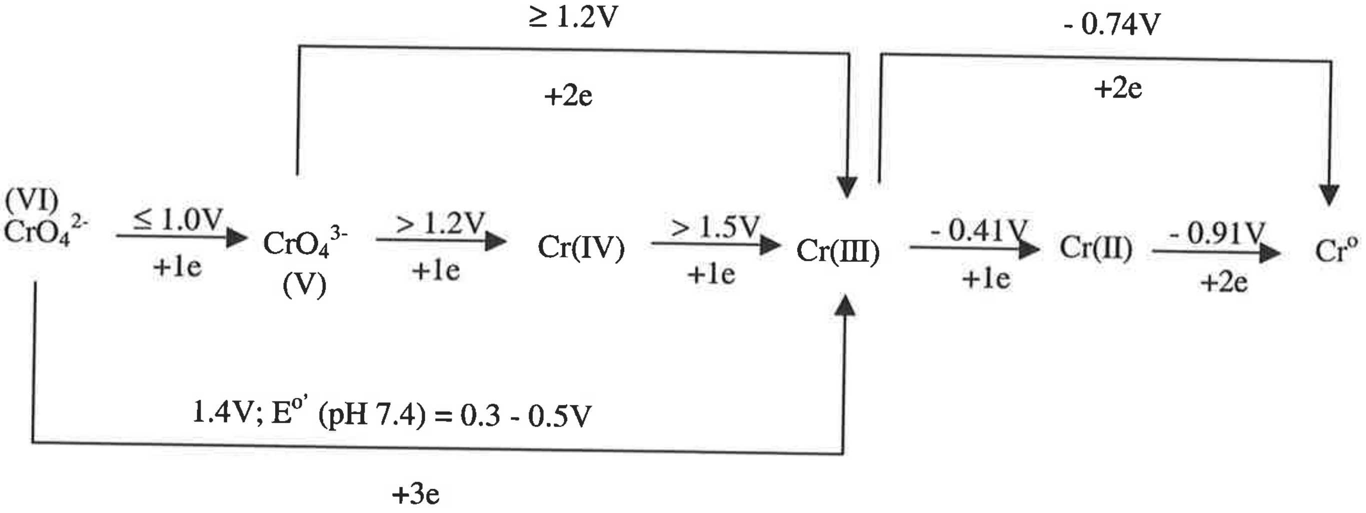

Fig. 2.1 Reduction potential diagram for chromium. (Source: Neiboer and Jusys, 1988)

2.2.3 Chromium (VI) Chemistry

Hexavalent Cr is a strong oxidizer and as a result exists only in oxygenated species that are very soluble and pH dependent according to the following equilibria (Nieboer and Jusys, 1988).

$$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4^- \text{ --------------------------- } \quad K_{a1} = 10^{\,0.6}$$

$$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-} \text{ -------------------------- } \quad K_{a2} = 10^{\,-5.9}$$

Because the pH in environmental matrices varies between 3-10 only $HCrO_4^-$ and CrO_4^{2-} are present in natural systems. Also, at concentrations of Cr(VI) greater than 0.01 M, dimerization of the chromate ion occurs (Baes and Mesmer, 1976) yielding the dichromate ion (Whitten and Gailey, 1984).

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow 2HCrO_4^- \text{ --------------------- } \quad K = 10^{-2.2}$$

In biological systems, the chromate concentrations encountered are likely to be considerably $<10^{-2}$ M and therefore the existence of dichromate is not expected to be significant, especially at physiologic pH (about 7 to 8).

2.2.3.1 Chemical Reactivity of the Chromate Ion

Chromic acid has been used extensively as an oxidizing agent in both organic and inorganic chemistry and comprehensive reviews on these subjects have been published by Wiberg, 1965; Espenson, 1970: Beattie and Haight, 1972. Discussing the oxidizing power of chromate, Nieboer and Jusys (1988) concluded that chromate is chemically unstable at physiologic pH values but does not decompose as easily as expected on the basis that it had a highly positive standard reduction potential and a biologic half-life in hours.

The chromate ion is said to be non-labile kinetically because it is difficult to displace the oxygen atoms from the chromate ion (CrO_4^{2-}). In contrast, the hydroxyl group of the monoprotonated form of chromate ($HCrO_4^-$) is more readily replaced. The chromate ion is more soluble than Cr(III).

2.2.4 Chemistry of Cr(III)

Trivalent Cr species are considered non-labile and ligand displacement is slow (hours to days at room temperature) compared to most metal ions ($10^{-9} - 10^{-3}$ seconds at room temperature) (Cotton and Wilkinson, 1980). It is because of this kinetic inertness, that many complex species of Cr(III) that can be isolated and are stable in solution. The hydrated Cr(III) ion, $Cr(OH_2)_6^{3+}$, is similar to other trivalent metal ions, such as Fe(III) and Al(III), and has the same tendency to hydrolyse. This is often accompanied by polymerization. Hydrolysis involves the conversion of a bound water molecule to the hydroxide ion and results in the release of a proton. Equilibrium measurements have identified the existence of the following species: $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_{3(S)}$, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and $Cr_4(OH)_6^{6+}$ (Smith and Martell, 1976; Baes and Mesmer, 1976; Connett and Wetterhahn, 1983).

2.2.5 Toxicity of Cr Forms

Of the two common valence states, Cr(VI), is both toxic and soluble, while the other, Cr(III), is non toxic and insoluble. In fact, in trace amounts Cr(III) is an essential component of human and animal nutrition (Mertz, 1969, Jeejeebhoy et al., 1977) and an essential activator of insulin. It is most notably associated with glucose metabolism. The chromate ion is a class A human carcinogen by inhalation and an acute irritant in living cells (Yassi and Nieboer, 1988). Of all the metal carcinogens, Cr exhibited properties most nearly consistent with a mutagenic initiation model (Loforth and Ames, 1978).

2.2.5.1 Plant, Animal and Human Toxicity of Cr(VI)

Chromate is toxic to both plants and animals because it is a strong oxidizing agent, corrosive and a potential carcinogen (National Research Council, 1974).

2.2.5.2 Toxicity to Plants and Microorganisms

It has been demonstrated that Cr is not an essential component of plant nutrition from plant growth studies in solution cultures with low levels of Cr (Huffman and Alloway, 1973). At the same time CrO_4^{2-} is reportedly toxic and toxicity effects were observed in plants at concentrations from 18-34 mg/kg dry wt (NAS, 1974). Skeffington et al., (1976) observed that barley crops could withstand a Cr spiked nutrient solution up to 5.0 mg/L as Cr(VI). At a concentration of 5.0 mg/L Cr(VI), a yield reduction of 75% was noticed. Generally the root concentration of Cr was more than the shoot concentration (Cary et al., 1977a&b and Losi et al., 1994). Mishra et al., (1997) also observed the tendency of Cr to accumulate in roots for a paddy crop grown under flooded conditions. Plant growth studies on tannery sludge treated soils under glasshouse conditions have shown Cr toxicity when sludge was applied at a rate exceeding 3 g/kg and a significant yield reduction was observed (Naidu et al., 2000c). Toxicity was attributed to the presence of Cr(VI) in the added sludge material. Similar observations of Cr toxicity have been reported for crops grown in tannery sludge amended soils in India (Sara Parwin Banu et al., 2000).

The adverse effects of Cr(VI) on microorganisms are also well documented. Wong and Trevors (1988) reviewed the toxic effects of Cr on bacteria and algae, while recently, Cervantes et al., (2001) reviewed the interactions of Cr with microorganisms and plants. Ross et al., (1981) found that 10-12 mg/L of Cr(VI) was inhibitory to most of the soil bacteria in liquid media, whereas at this level Cr(III) had no effect. Two Cr(VI) resistant bacteria have also been recently isolated from the tannery waste contaminated site at Adelaide and studied for Cr(VI) toxicity. It was found that the growth of *Arthrobacter sp.* was not affected up to 50 mg/L of Cr(VI) whereas 10 mg/L was toxic to *Bacillus sp.* (Megharaj et al., 1999).

2.2.5.3 *Toxicity to Animals and Human Beings*

Acute exposure of rats to Cr(VI) by various routes of administration affected main target organs including liver and kidneys (U.S. EPA, 1980). Soluble chromate salts are highly toxic when administered intravenously (through the blood vein), with an LD50 of 10 – 50 mg/kg as compared with LD50 values of 200 – 350 and 1500 mg/kg obtained with dermal and oral exposure respectively (Carson et al., 1986). Conversely, oral administration of Cr(III) compounds are relatively non toxic. From feeding studies with rats and mice, an oral LD50 value of 1.87 and 3.25 g/kg was calculated for $CrCl_3$ and $Cr(NO_3)_3$ respectively (Smyth et al., 1969). The oral LD50 of $Na_2Cr_2O_7$ in humans has been reported to be 50 mg/kg (NIOSH, 1979). Other effects of Cr(VI) poisoning include gastric distress, olfactory sense impairment, nosebleeds, liver damage and yellowing of the tongue and teeth. Systemic toxicity may occur in both of the oxidation states, mainly due to increased absorption of Cr through the broken skin resulting in renal chromate toxicosis, liver failure and eventually, death (Lippmann, 2000).

2.2.5.4 Carcinogenicity and Genotoxicity Effects

The carcinogenicity of Cr in experimental animals is well documented (see for example reviews in IARC, 1980, 1990; Cohen et al., 1993; Costa, 1997; Cohen and Costa, 1997). These studies also support the hypothesis that some of the most potent carcinogens are the slightly insoluble hexavalent compounds.

The Cr(VI) ion is readily taken up into eukaryotic cells by anion-carrying proteins, after which it is reduced to Cr(III) by a number of cytoplasmic reducing agents. The reduction of Cr(VI) to Cr(III) causes the generation of oxygen radicals in cells that, in and of themselves, can produce DNA damage. Additionally the Cr(III) that is eventually formed can become adducted to the DNA. Recent studies have shown that Cr(VI) is very potent in forming DNA-protein crosslinks. This involves the binding of Cr(III) to the phosphate backbone of DNA and crosslinking a protein to the DNA strand (Lippmann, 2000). These cross links are likely to have mutagenic consequences and are probably more significant in determining the mutagenicity of Cr than the oxidative DNA damage produced by oxygen radicals generated during the reduction of Cr(VI) to Cr(III). The earlier sections elucidated the general chemistry of Cr, oxidation states and toxicity of forms to the environment. In the following sections a brief account of the chemistry of Cr in soil and water and the implications of Cr contamination in the soil environment is discussed.

2.2.6 Chemistry of Cr in Soil

The concentrations of Cr in soils are determined by the amount present in the parent materials from which the soils form, plus the amounts added through wind, water and human activities, minus the amounts removed through leaching, surface runoff, volatilisation and uptake by vegetation. In the literature a number of reviews are available on the chemistry of Cr in soil and water that describe in detail the factors that influence the transformations between the two stable Cr species of Cr(VI) and Cr(III) in soils (Cary, 1982; Bartlett and James, 1988; Fendorf, 1995; Proctor et al., 1997; Naidu and Kookana, 2000). The important reactions of Cr in soil and water are summarized in Fig. 2.2, which describes the Cr cycle in soil and water.

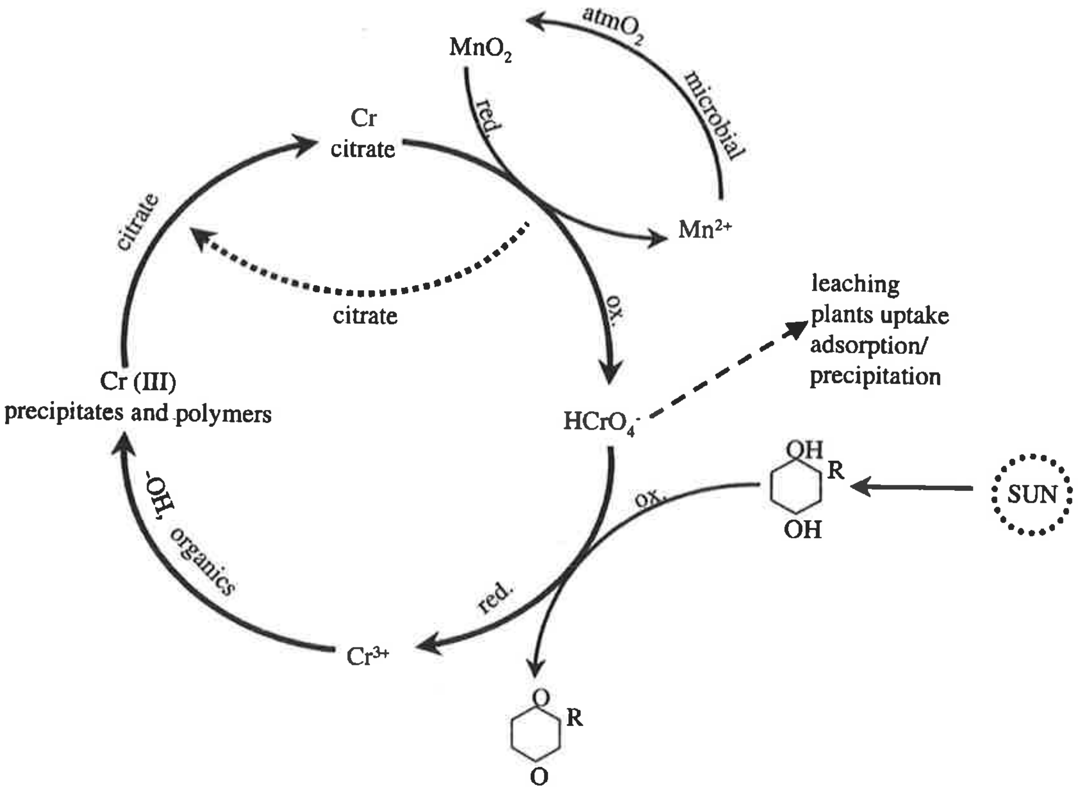

Fig. 2.2 Chromium cycle in soil and water (modified from Bartlett and James, 1988)

2.2.6.1 Chromium Cycle in Soil and Water

In soil the predominant species of Cr is Cr(III), although Cr(VI) is also commonly found in soils. Because Cr(VI) has proven to be the more toxic species and reduction reactions are more favoured in most soil environments the starting point for the Cr cycle can be Cr(VI).

The chromate ions in soil solution are, $HCrO_4^-$ or CrO_4^{2-} depending upon the soil pH. Chromium can be temporally removed from the soil by adsorption/precipitation reactions, uptake of plants or leached to subsurface layers if the soil pH and moisture conditions are favourable. Some of the Cr(VI) will undergo the next step in the cycle, reduction of Cr(VI) to Cr(III), by carbon reduced by the sun's energy through photosynthesis. An intermediate species in soil, such as Fe^{2+} or S^{2-}, and microbial decomposition of soil organic matter can serve as direct electron donors. Bartlett and James (1988) refer to this step as "dechromification" and is the vital segment of the Cr cycle. In terms of decontamination, this step is also vital because the toxic form of Cr is reduced to the non-toxic form. Thus reduced Cr(III) is bound by a variety of ligands in soil solution that render it insoluble, immobile and unreactive. Mobile ligands such as citrate extract Cr(III) and deliver it to MnO_2 surfaces where both organic and Cr become oxidised. The MnO_2 surface is formed by the oxidation of Mn by atmospheric O_2 or soil microbes. Sometimes the ligand is recycled because the Mn(III) formed by reverse dismutation picks up its electrons from the Cr(III) in preference to those from the organic ligand and only Cr is oxidised. When organic ligands are excessive they tend to induce reverse dismutation of MnO_2 by binding the Mn(III) and this Mn(III)-organic complex may prevent formation of Cr(VI) or reduce it as fast as it forms, short circuiting the cycle or speeding up the cycling gyrations (Bartlett and James, 1988).

For the present study much attention was directed towards the first step of the Cr cycle, i.e., partitioning of Cr in soil fractions, soil solution factors influencing the adsorption and desorption of Cr(VI) and the reduction of Cr(VI) to Cr(III) in soils. In the following sections the first reactions of the Cr cycle involving both Cr species are reviewed and the implications to tannery waste contaminated soil are discussed.

2.2.7 Solid Phase Speciation of Cr in Native Soils

Soils derived from serpentines usually contain higher concentrations of Cr and nickel (Ni). Noble and Hughes (1991) used a sequential extraction scheme of 0.5 M KNO_3 for 16 h; deionised water for 2 h (repeated three times and the data combined); 0.5 M NaOH for 16 h; 0.05 M Na_2EDTA for 6 h and finally 4 M HNO_3 for 16h at 80°C to extract various soil fractions of Cr and Ni in serpentine soils from two sites of eastern Transvaal, South Africa. In all of the 9 soils studied 95% of the total Cr was extractable by HNO_3, whereas the general order of the remaining extractants was NaOH > EDTA >> $KNO_3 + H_2O$ (Fig. 2.3).

In another study Xiao-hou et al., (1993) extracted fractions of Cr in 25 representative soils from the whole of China using a different sequential extraction scheme (Table 2.1). The total Cr in the soils varied from 24 to 110 mg/kg and in the fractions, 81.5% of Cr was found in the residual fraction followed by 9.8% in crystalline Fe oxide fractions. All other fractions combined accounted for 10.84% of Cr.

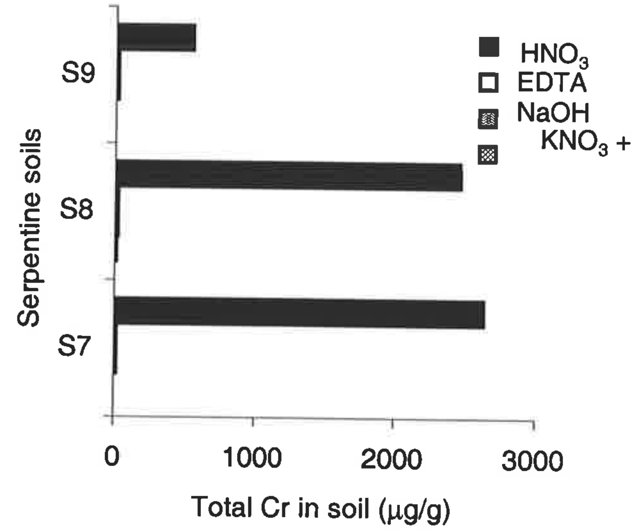

Fig. 2.3. Fractions of Cr in three serpentine soils (Data source, Noble and Hughes, 1991)

Table 2.1 **Sequential extraction scheme to fractionate Cr in 25 Chinese soils**

Step	Fraction	Extractant	Soil:solution	Equilibrium Conditions
1	Exchangeable	1M $Mg(NO_3)_2$ (pH 7.0)	1:4	Shake 2 h, 25°C
2	Carbonate	1M NH_4OAc (pH 5.0)	1:10	Shake 6 h, 25°C
3	Mn oxide bound	0.1M $NH_2OH.HCl$ (pH 2.0)	1:10	Shake 1 h, 25°C
4	Organically bath bound	a) 30% H_2O_2 added in two times b) 1M NH_4OAc (pH 5.0)	1:10 1:10	a) Dry by water (85°C) then cool b) Shake 2 h, 25°C
5	Amorphous Fe oxide	0.2M $(NH_4)_2C_2O_4$+ 0.2M H2C2O4	1:20	Shake 4 h in dark, 25°C
6	Crystalline 96°C Fe oxide	0.2M $(NH_4)_2C_2O_4$+ 0.2M ascorbic acid	1:20	Water bath 1 h,
7	Residual	Digest with HF-$HClO_4$		

Source: Xiao-hou et al., 1993.

2.2.8 Chromium Fractions in Sludge and Sludge Amended Soils

Sequential extractions studies on Cr in soil fractions are designed primarily for sludge amended / contaminated soils rather than native soils. A sludge high in Cr and Zn was added to a loamy sand soil and over two years Dudka and Chlopecka (1990) studied the partitioning of Cr in the different soil fractions. The sequential extraction scheme of exchangeable ($CaCl_2$), carbonate (NaOAc), Fe-Mn oxides ($NH_2OH.HCl$), organics ($HNO_3 + H_2O_2$) and residual ($HF + HClO_4$) developed by Tessier et al., (1979) was followed. Predominantly Cr was partitioned in the organic fraction of the sludge and sludge treated soil (Fig. 2.4). However, in the untreated soil more was partitioned in the residual fraction. Exchangeable and carbonate bound Cr was negligible compared to total Cr.

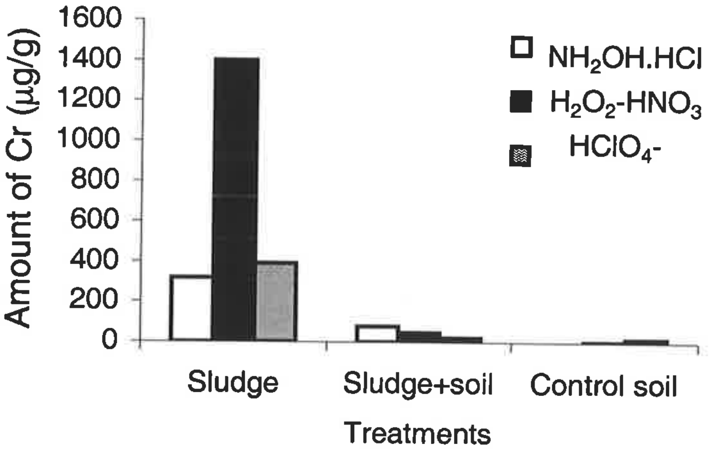

Fig. 2.4 Partitioning of Cr in sludge, sludge treated and normal soils (Data source: Dudka and Chlopecka, 1990)

The solid phase speciation of 13 metals including Cr in sewage sludge from an urban wastewater plant in Spain was studied using the sequential extraction scheme of Tessier et al., 1979 by Zufiaurre et al., (1998). Partitioning of Cr was found mostly in the organic matter fraction (46%) followed by the residual fraction (40%). The average amount of total Cr present was 785 mg/kg and the sludge had an average organic matter content of 48.4%. Similar results were also observed by Fernandez Albores et al., (2000) for urban sewage sludge. However, they compared the sequential extraction scheme of Tessier et al., (1979) and a recent method developed by the Community Bureau of References (BCR) (Quevauviller et al., 1993).

Partitioning of Cr in native soils clearly indicates that most of the Cr is strongly bound to the residual fraction while in sludge and sludge-amended soils it is predominantly bound to the organic fractions. Water soluble and exchangeable Cr fractions are negligible in native and sludge amended soils.

2.2.9 Chromium Fractions in Soils Contaminated by Industries

From the literature it was found that few studies have examined the fractionation of Cr from soils collected from former industrial sites. A clay loam, loam and sandy clay loam soil were collected from a heavy metal contaminated site and Wasay et al., (1998) studied the fractionation of Cr only in the clay loam soil using the sequential extraction scheme proposed by Fiedler et al., (1994). Out of the total 832 mg/kg of Cr, 486.9 mg/kg (59%) was bound to the organic fraction of the soil.

Phillips and Chapple (1995) used the sequential extraction scheme of Tessier et al., (1979) to fractionate Cr along with other metals from a soil collected from a former industrial site within inner Brisbane. Past activities at the site-involved shipbuilding and a government poisons store. Chromium concentrations in all soil fractions were low and approximately 80% of the Cr was associated with organic and oxide fractions, with negligible concentrations detected in the exchangeable and carbonate fractions.

In another study (Maiz et al., 1997) soil samples collected from a polluted mine works, steel factory and by highway emissions were sequentially extracted to find the partitioning of Cr and other metal fractions in these soils. A short three-step sequential extraction scheme was compared with a modified Tessier et al., (1979) method and modified Ure et al., (1993) method. Since different extractant concentrations were used for the three different methods comparison of the results was difficult. However, Cr was predominantly partitioned in the residual fraction of the soils in all of the three methods.

In all of the above studies Cr fractionation was investigated together with a range of other metals and the concentration of Cr was not very high in the soils studied. In the following section sequential extraction studies specifically targeting Cr in highly Cr contaminated soils are reviewed.

Additionally, although there was good agreement between the sum of various fractions with the total amount of Cr present, in all of the above Cr fractionation studies great importance was not given to the speciation Cr into Cr(III) and Cr(VI).

2.2.10 Partitioning of Cr in High Cr Contaminated Soils

The fractionation and oxidation of Cr in tannery waste and sewage sludge amended soils was studied by Milacic and Stupar, (1995). The following sequential extraction scheme was used to study the partitioning of Cr in soils, sludge and sludge-amended soils (Table 2.2). This sequential extraction scheme is significantly different from the extraction schemes used to fractionate Cr in soils as mentioned in Sections 2.2.7 to 2.2.9. Use of 0.015 M KH_2PO_4 for water soluble Cr is appropriate for targeting the Cr(VI) in Cr contaminated soils. However, Bartlett and James (1979) showed that a 0.01 M phosphate buffer is more suitable for extracting the exchangeable Cr(VI) in

Table 2.2 **Sequential extraction scheme to fractionate Cr in soil, tannery sludge and sludge-amended soils**

Step	Fraction	Extractant	Equilibrium Conditions
1.	Water soluble	0.015M KH_2PO_4	Shake 2 h
2.	Exchangeable	1M NH_4Cl	Shake 4 h
3.	Organic bound	0.1M $Na_4P_2O_7$	Two extraction, 4 and 18 h
4.	Carbonate bound	1M $NaCH_3COO$ pH 5	Two extraction, 4 and 18 h
5.	Oxides and hydroxides	0.04M $NH_2OH.HCl$ in 25% v/v acetic acid pH 2	Two extraction, 90°C 5 h
6.	Chromium sulphide	1M HNO_3	Two extractions, 4 and 18 h
7.	Residual	$HNO_3 + HClO_4 + HF$	

Source: Milacic and Stupar, (1995).

soils. Hence, use of 0.015 M KH_2PO_4 for water soluble fraction might overestimate the water soluble fraction by extracting Cr(VI) as well from the adsorbed phase.

Fractionation of Cr in natural soils showed that most of the Cr (80%) was bound to the residual fraction in clay and sandy soils. In peat soils while substantial amounts of Cr (20%) were bound to the organic fraction the majority of the Cr (70%) was still found in the residual fraction. The water soluble and exchangeable fractions were very low for all of these three soils. The fractionation of Cr in tannery sludge showed an entirely different partitioning trend for Cr where over 65% of the Cr was bound with oxides and hydroxides. About 20% of the Cr was bound to organic matter and 13% existed as carbonates. Compared to natural soils, substantially more water-soluble (1.5%) and exchangeable (0.5%) Cr was extracted from tannery sludge. The concentration of total Cr was very high in the sludge - about 30000 μg/g. The partitioning of Cr in tannery sludge amended clay and sandy soils was similar to that of Cr partitioning observed for the sludge. However, in peat soil Cr was bound primarily to the organic fraction (35%) followed by oxides and hydroxides (25%) and the residual fraction (20%).

In another study Chuan and Liu (1996) sequentially extracted Cr using the Tessier et al (1979) scheme from pig tannery sludge obtained from tannery plants representative of Taiwan. Out of the total 1.7 x 10^4 mg/kg of Cr, 93% of Cr was bound to the Fe-Mn oxides followed by organic and residual fractions. Chromium in the exchangeable fraction was negligible compared to total Cr. However, speciation of Cr was not carried out in this study.

In Cr contaminated aquifer sediments Asiakinen et al., (1994) studied the partitioning of Cr using a different sequential extraction scheme. The scheme was composed of exchangeable (0.01 M KH_2PO_4/K_2HPO_4 (1/1) solution (at pH 7.2), organic (0.1 M $Na_4P_2O_7$ at pH 10), Fe/Mn oxide (0.1 M $NH_2OH.HCl$ in 25% acetic acid (v/v) pH 2) and residual (reflux with HNO_3 and H_2O_2). Along with the basic sequential scheme, and in order to dissolve freshly formed Cr precipitated during the organic (0.1 M $Na_4P_2O_7$ at pH 10) extraction, 10 mL of 0.05 M HCl was equilibrated for 30 minutes before the Fe/Mn step. Out of the 346 mg/g of total Cr in the soil, 25% was in an exchangeable form, 11% was bound to organic matter, 30% was bound to Fe/Mn oxide and 34% was tightly bound to the soil matrix.

More recently Thangavel and Naidu (2000) sequentially fractionated Cr from the tannery waste contaminated soils up to a depth of 70 cm, with an increment of 10 cm from the surface, from Mount Barker, Australia. They used a modified sequential extraction scheme as used for serpentine soils by Noble and Hughes (1991). The scheme was: water-soluble fraction (deionized water – repeated 3 times), exchangeable (0.5 M KNO_3), organic (0.5 M NaOH), remaining organic plus Fe oxide (0.05 M Na_2EDTA) and residual (4 M HNO_3). The total Cr concentration was in the range 17529 – 61931 mg/kg for first 10 cm in the three soil profiles. Over 90% of the Cr was partitioned in the residual fraction and the order of partitioning was Fe oxide > organic > exchangeable = water. Chromium speciation was carried out for water soluble, exchangeable, organic and Fe oxide fractions and it was found that significant concentrations of Cr(VI) were in the water soluble and exchangeable fractions.

2.2.11 Partitioning and Mobility of Cr

The solid phase speciation studies clearly indicated that at a low level of Cr concentration either in natural or contaminated soils, most of the Cr is partitioned in the residual fraction. In highly organic soils a significant portion of Cr is partitioned in the organic fraction and equally partitioned either in Fe oxide or residual fractions. The concentration of Cr in water soluble and exchangeable fraction is very low and indicates low mobility of Cr from these soils.

Although in highly contaminated soils while Cr partitioning is found predominantly in the organic and Fe oxide fractions, a significant amount of Cr is seen in water soluble and exchangeable fractions. In terms of bioavailablity these two fractions are important and, given that Cr exists in two stable oxidation states, speciation of Cr requires further attention. For the exchangeable fraction a 10 mM phosphate buffer proves to be a suitable extractant, but the efficiency of potassium in a K_2HPO_4/KH_2PO_4 buffer to extract exchangeable Cr(III) was not tested. It may be necessary to investigate exchangeable Cr(III) because once soil pH conditions are favourable, and in the presence of MnO_2, this fraction could be available in the soil solution to effect oxidation of Cr(III) to the toxic Cr(VI) in soils. Milacic and Stupar (1995) used 1 M NH_4Cl for the exchangeable fraction and 0.015 M KH_2PO_4 for water-soluble fraction of Cr in soils. However, information on easily labile pools and exchangeable pools of Cr(VI) in contaminated soil may be helpful in understanding the desorption chemistry of Cr(VI) and to devise a suitable remediation strategy to decontaminate the soil. Hence, these issues were addressed in the sequential extraction scheme used in the present study.

2.2.12 Factors Affecting Soil Solution Chemistry of Cr

The presence of Cr in soil solution is determined by many soil factors, namely, pH, redox potential, type of clay minerals, organic matter content, nature of adsorbed phase, soil solution composition and, importantly, the form of Cr added from the source of pollution.

2.2.12.1 Soil pH

The phase diagram depicting the thermodynamic stability of aqueous Cr species over a range of pe (redox) and pH is presented in Fig. 2.4 (Calder, 1988).

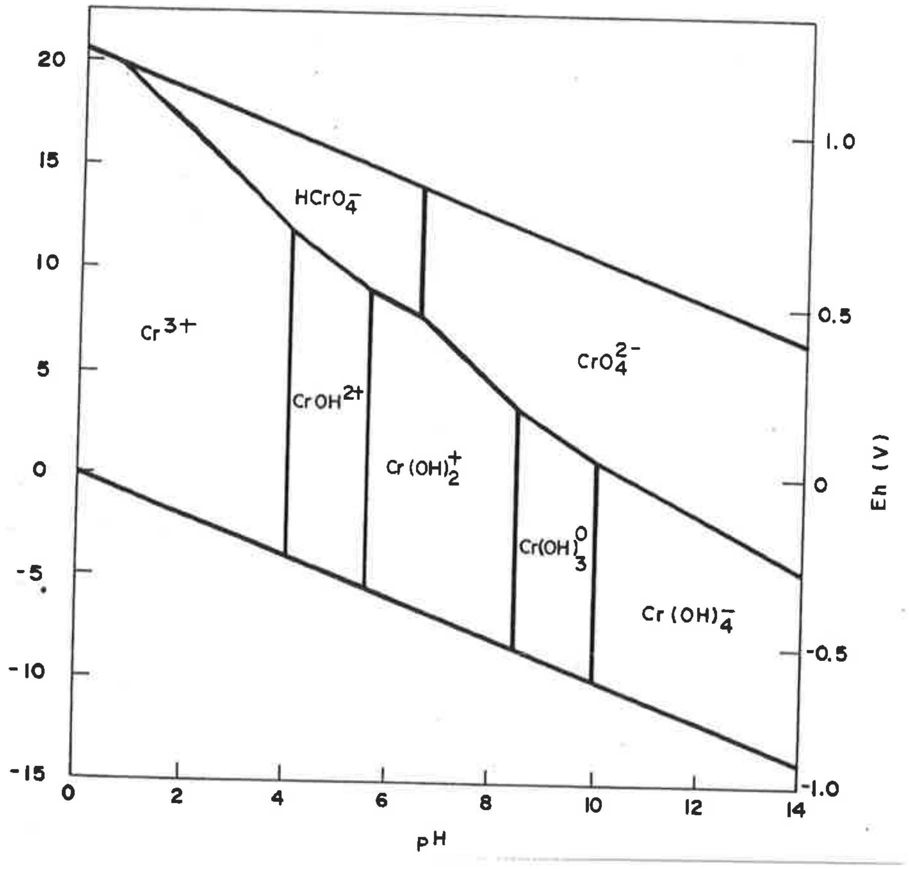

Fig. 2.4 Thermodynamic stability of aqueous Cr species over a range of pe and pH encountered in the surface environment (Source: Calder, 1988)

The Cr(III) form is the most stable form under reduced (low redox) conditions and is present as a cationic species with the first or second hydrolysis products dominating at pH values from 4 to 8. Under oxidised (high redox) conditions Cr(VI) is often the thermodynamically most stable species observed in the pH range of 2 to 14. However, Cr(VI) is readily reduced to Cr(III) in the presence of reducing agents and

Cr(III) can form highly soluble organic complexes under acidic conditions (Calder, 1988).

2.2.12.2 Chromium (III) in Soil Solution

The dominant species of Cr(III) in water with a pH between 6 and 8 is $Cr(OH)_2^+$. In acidic waters $CrOH^{2+}$ and Cr^{3+} predominate and $Cr(OH)_3^o$ and $Cr(OH)_4^-$ are predominate in alkaline waters. The governing reactions are:

$$Cr^{3+} + H_2O \Leftrightarrow CrOH^{2+} + H^+$$

$$CrOH^{2+} + H_2O \Leftrightarrow Cr(OH)_2^+ + H^+$$

$$Cr(OH)_2^+ + H_2O \Leftrightarrow Cr(OH)_3^o + H^+$$

$$Cr(OH)_3^o + H_2O \Leftrightarrow Cr(OH)_4^- + H^+$$

Cr(III) complexes with many organic ligands, as well as fluoride, ammonia, cyanide, thiocyanate, oxalate, and sulphate (Baes and Mesmer, 1977).

Bartlett and Kimble (1976a) studied the behaviour of 10 mmol/kg Cr(III) added to a spodic horizon, a Spodosol Ap horizon, and a clay Alfisol A horizon. Soils had a pH in the range of 4 – 4.8. They also studied the effects of increasing pH levels adjusted with $CaCO_3$ and extraction with pH 4.8 NH_4OAc, 1 M HCl, 1 M NaF and 0.12 M $Na_4P_2O_7$. The results indicate that only HCl and $Na_4P_2O_7$ extracted significant portions of the Cr(III) added. The NH_4OAc and NaF removed very small fractions of the total amount present. In two Spososols, as characterized by the NH_4OAc and NaF extracts, Cr(III) decreased as the pH was increased by addition of $CaCO_3$ and the effect was similar in clay soils for NH_4OAc but not for NaF. It was inferred that as the pH of the studied soils was increased, the extractability of Cr(III) decreased.

In the same study, Bartlett and James (1976a) considered the pH and solubility relationship of Cr(III) in a silty loam soil and solution by raising the pH by addition of $CaCO_3$ or NaOH. As solution pH was raised above 4, the solubility of Cr(III) decreased, with apparent complete precipitation occurring at pH 5.5. They presumed that the precipitate was made up of macromolecules with Cr ions in six-coordination complexes with water and hydroxy groups (Mertz, 1969). Grove and Ellis (1980) observed a similar relationship for Cr(III) solubility and pH. When Cr(III) precipitates as amorphous $Cr(OH)_3$, the expected concentration of aqueous Cr(III) would be less than 0.05 mg/L (Rai et al., 1989).

In studies conducted by Cifuentes et al., (1996), different amounts of Cr(III) were added as $CrCl_3.6H_2O$ to slightly acidic (pH 6.2) and two alkaline soils (pH 7.9 and 8.3). They found that higher concentrations of Cr(III) were observed in solution where higher Cr(III) concentrations were used. This was the result of low equilibrium soil pH (<3.8) at the end of the experiment and MINTEQA2 predicted no precipitation of Cr(III) and the aqueous speciation was dominated by Cr^{3+} and $Cr(OH)^{2+}$. In our studies in the long term tannery waste contaminated soils we observed the presence of soluble Cr(III) in the water extracts from subsurface horizon (> 50 cm) having an acidic pH of 4 and enhanced release of Cr(III) was also observed when extracted with 0.01 M $CaCl_2$ (Avudainayagam et al., 2001). Although the presence of Cr(III) in soil solution is highly pH dependant, the studies in long term tannery contaminated soil indicated that the effect of aging favours stronger binding of Cr(III) to adsorption sites in soil.

2.2.12.3 Solubility of Organically Complexed Cr(III)

The solubility of Cr(III) from the inorganic or organic pool makes it available for further sorption or available for oxidation reactions to form toxic Cr(VI). Based on our present knowledge, and the extremely low solubility of $Cr(OH)_3$ at pH >5.5, it is evident that leaching of Cr(III) to ground water or oxidation of Cr(III) to Cr(VI) is rare in soils. However, problems of pollution could arise with organically complexed Cr(III) which is mobile in soils.

James and Bartlett (1983a) studied the relationship of pH, organic ligands and Cr(III) behaviour by using different naturally occurring carboxylic acids (citric acid)~~and diethylenetriamine pentaacetic acid (DTPA))~~ found in soils and roots. They found that Cr(III) in citric acid remained soluble up to pH 7 - 7.5, whereas Cr(III) in water (no organic ligand added) was precipitated between pH 4.5 - 5.5. The solubility of Cr(III) in DTPA was similar to that in citric acid except that Cr(III) in DTPA was less soluble than Cr-citrate at a pH between 6 and 7. They also studied the complexation of Cr(III) by organic polymers such as fulvic acid and water soluble organic matter leached from an air dried soil sample. Fulvic acid effectively complexed Cr(III) and prevented its precipitation up to approximately pH 7.5, if the ratio of fulvate-COOH/Cr = 1.

James and Bartlett (1983a) also studied the long term solubility of inorganic and organically complexed Cr(III) in soils at different pH. In their incubation experiments, they observed that water soluble Cr(III) decreased rapidly during the first week regardless of whether it was added as Cr citrate or $CrCl_3$. However, during the following 7 weeks, soluble Cr(III) in the citrate treatments decreased slowly compared with the inorganic $CrCl_3$. Soluble Cr(III) could be seen even after one year of incubation, when applied in Cr-citrate form regardless of soil pH.

Fractionating Cr in tannery sludge Milacic and Stupar (1995) observed a significant concentration of water soluble Cr (450 µg/g) and out of this water soluble fraction only a very low concentrations of Cr(VI) was found (0.9 µg/g). This suggested that most of the water soluble Cr was Cr(III) but details on the pH of the tannery sludge used was not reported. However, Naidu et al., (2000c) reported a pH range of 7.71 – 9.44 for the tannery sludge collected from a tannery in South Australia. Hence, it may be concluded that even in alkaline pH, organically complexed Cr(III) could be available in soil solution.

2.2.12.4 Adsorption / Desoprtion of Cr(III)

Cr(III) sorption and release reactions are important for determining the availability of soluble Cr forms for further oxidation to toxic Cr(VI) in soils.

Cr(III) was shown to be sorbed strongly on to soil minerals, to be bound to soil organic matter and to form mineral precipitates (Bartlett and Kimble, 1976a; Cary et al., 1977a; Rai et al., 1987; Bartlett and James, 1988; Rai et al., 1989; Palmer and Witbrodt, 1991; Losi et al., 1994). Sorption of Cr(III) was also reported to decrease when other inorganic cations or dissolved organic ligands were present in solution.

Fendorf et al. (1994a,b) studied the mechanism of Cr(III) sorption on silica using extended absorption fine structure spectroscopy. Cr(III) formed a monodentate surface complex on silica. Arnfalk et al. (1996) studied the Cd, Hg, Pb, Cr(III) and Cr(VI) retention in 14 different types of minerals and soil materials based on pH dependency and other soil physico-chemical parameters. The results verified the importance of geochemical parameters of soils such as organic content, type of clay mineral, presence of complexing ions, and redox potential for controlling metal uptake.

Montmorillonite (in bentonite and smectite) showed the highest retention of Cd, Cr(III) and Pb among all minerals and soil materials, whereas illite and kaolinite showed lower retention than the soils. The clay mineral montmorillonite showed highest retention because it had the highest surface activity (Kashef, 1986).

The difficulty in displacing Cr from smectite indicates that the Cr is bonded specifically. If Cr were held only through outer sphere complexes, the smallest hydroxy polymers would be readily displaced by Ca (Dubbin and Goh, 1995). Drljaca et al. (1992) found that, while the montmorillonite was still wet, the adsorbed Cr could be easily exchanged with other cations. However, upon drying the Cr became virtually non-exchangeable. These authors suggested that as the interlayer region collapsed due to loss of water, the Cr came in to close contact with the siloxane surface allowing inner-sphere complexes to form. Transition metals of the d^3 type must overcome a large energy barrier in the formation of intermediates. Ligand displacement reactions of Cr(III) complexes are extremely slow (Cotton and Wilkinson, 1988). Cr(III) is held strongly, typically through covalent bonds, and its displacement is extremely difficult through simple exchange reactions. However, the potential for Cr(III) to be oxidised to the more toxic Cr(VI) form is of some concern because of the instability of covalent bonding under strong oxidising conditions.

Both adsorption and precipitation reactions as well as specific and non-specific reactions are possible for the retention of Cr(III) in soils. However, organically complexed Cr(III) could be available to soil solution even at high soil pH and may effect the oxidation of Cr(III) to toxic Cr(VI) in soils.

2.2.13 Oxidation of Cr(III) to Cr(VI)

Although this is one of the most important reactions in the soil, where the non toxic from of Cr(III) is oxidised to toxic Cr(VI), only a brief review of the reaction is discussed here because of the objectives of the study.

Oxidation of Cr(III) to Cr(VI) represents a significant environmental hazard because a relatively nontoxic species is transformed into toxic one. Manganese oxides have proven to be the only naturally occurring oxidant of Cr(III). Oxidation of Cr(III) in the presence of MnO_2 was first observed by Bartlett and James (1979) who noted that Cr(VI) was present in the effluents of most soils reacted with Cr(III). Even the manganese oxide with the highest zero point of charge and the most crystalline structure, pyrolusite, is an effective oxidant of Cr(III) (Eary and Rai, 1987; Saleh et al., 1989).

Adsorption of Cr(III) by Mn oxides is possibly the first step in its oxidation by Mn. Manganese oxides typically accumulate on the surface of clay and iron oxides at relatively high redox potentials in soils. McKenzie (1977) pointed out that Mn minerals have large surface areas and tend to have high negative charge at all but extremely acidic pH. These properties are associated with high adsorptive capacities, particularly for heavy metals. Cr(III) can be oxidised to the Cr(VI) form in the presence of Mn^{4+}. Mn^{4+} serves as the oxidising agent and is reduced to Mn^{2+}, as shown in the equation

$$2Cr^{3+} + 3MnO_2 + 2H_2O -\Leftrightarrow 2CrO_4^{2+} + 3Mn^{2+} + 4H^+$$

2.2.13.1 *Effect of pH*

Bartlett and James (1979) studied the influence of pH from 3-10 on Cr(III) oxidation in a soil having 1200 mg/kg of 1 M HCl extractable manganese. The study was carried out by shaking the soil for 0.5 min out of every 2 min for 18 h. They observed that at pH 3.2 all of the Cr(III) was oxidised to Cr(VI) and about one fourth of the Cr(VI) formed was adsorbed to the soil. The oxidation and adsorption decreased with increasing pH. The percentage of Cr(III) oxidation to Cr(VI) decreased from 100 to 30 at pH 6 and stayed constant at 30 up to pH 9. They used a large solution:soil ratio (2000:1) to control the change in pH due to addition of $CrCl_3$ to the soil.

2.2.13.2 *Solubility of Cr(III) and Oxidation*

Solubility and availability of Cr(III) in soil solution is critical for the oxidation of Cr(III) to Cr(VI) in soils. Although at soil pH > 5.5 Cr precipitates as $Cr(OH)_3$ and decreases the solubility, Cr(III) complexed by some low molecular weight organic acids such as citrate and gallic acid increases the solubility and mobility even at higher pH, thereby facilitating its oxidation.

James and Bartlett (1983b) compared the oxidising tendencies of four forms of Cr(III) added to a field moist soil and incubated for 15 days. The four forms were, freshly precipitated $Cr(OH)_3$, Cr-citrate, aged $Cr(OH)_3$ and aged $Cr(OH)_3$ with citrate. The maximum Cr(VI) levels observed decreased in the order: freshly precipitated $Cr(OH)_3$ > Cr-citrate > aged $Cr(OH)_3$ in citrate > aged $Cr(OH)_3$.

Recently, Milacic and Stupar (1995) studied the oxidation of Cr(III) in tannery waste amended to three soil types. The results of their fractionation study showed that 5 months after the start of the experiment, up to 1.1% of the total added Cr was oxidized in clay, 0.45% in sand and only 0.03% in peat soil. The degree of Cr(III) oxidation was found to be proportional to the concentration of manganese (IV) oxides and water soluble Cr(III) in the soils. They observed a decrease in the concentration of water soluble Cr and Cr(VI) on continuance of the experiment because Cr was redistributed to more sparingly soluble fractions.

2.2.14 Factors Affecting Soil Solution Cr(VI)

The pe-pH stability phase diagram (Fig. 2.4) illustrates the dominant aqueous Cr(VI) species present under equilibrium conditions. Under oxidising conditions and from pH 2 – 14 anionic Cr (VI) dominates. The $HCrO_4^-$ species of Cr(VI) dominates up to pH 6 and > pH 6 it dissociates to form CrO_4^{2-} in dilute aqueous systems (Deltcombe et al., 1966). In the soil solution the concentration of Cr(VI) is dependent on soil pH, redox potential, adsorption/desorption processes, competing ions in soil solution, reduction reactions and the nature of the Cr(VI) from the pollution source.

2.2.14.1 Effect of pH

The soil solution pH plays a significant role in the availability and mobility of Cr(VI) in soil. Soil pH affects the quantities of positive and negative charges on soil colloids, especially on organic matter and on Fe(III), Al(III), and Mn(III,IV) oxides (McKenzie, 1977; Parfit, 1978). Binding of Cr(VI) species in soils will depend on soil mineralogy and on the relationship of soil pH to the pH of zero point of charge of the colloids involved. Because of its anionic nature, Cr(VI) is not retained appreciably on negatively charged colloids of soils or sediments. However, Cr(VI) is attracted to positively charged surfaces, such as iron, manganese and aluminium oxides and hydroxides (Stumm and Morgan, 1981).

Bloomfield and Pruden (1980) studied the leaching behaviour of Cr(VI) in near neutral (6.65) and acidic (4.2) soils from the Sawyers field of the Rothamsted Experimental Farm and found that in neutral soils, after three weeks of contact, most of the Cr(VI) was removed unchanged by leaching water. Although reduction of Cr(VI) was a major factor with the acid soils, about half the added Cr(VI) persisted in sorbed or labile forms. These observations demonstrated the potential for Cr(VI) leaching in alkaline soils. Indeed, Naidu et al., (2000b) and Mahimairajah et al., (2000) presented evidence of Cr(VI) in ground water from highly Cr contaminated alkaline soils.

From their batch leaching experiments on a chromite ore processing waste contaminated soil from New Jersey, Weng et al., (1994) reported that at $pH < 2.5$, the amount of Cr(VI) leached was below the detection limit (0.01 mg/L). Between pH 2.5 and 4.5, the amount of Cr(VI) leached sharply increased and reached a maximum release at pH 4.5. The amount of Cr(VI) leached remained constant between pH 4.5 and 12. They attributed this to adsorption of Cr(VI) onto the soil under acidic conditions. The pH_{zpc} of the studied soil was 6.8 and electrostatic interactions favour anionic chromate species adsorption when solution pH is less than pH_{zpc}; electrostatic chromate adsorption onto Cr-soil is not favorable at a high solution pH.

Davis and Olsen (1995) studied the adsorption of Cr(VI) on to two sandy soils by mixing the soil with groundwater spiked with various concentrations of Cr(VI). They observed low Kd (Freundlich adsorption constant) values of 0.16 and 0.21 L/kg for the two soils and attributed this result to competition by SO_4^{2-} present in the groundwater for the adsorption sites, a process which enhanced the Cr(VI) release in these neutral pH soils. Henderson (1994) measured an average Kd_{Cr} of 0.31 L/kg for Trinity sand aquifer material of pH 7.5. However, Stollenwork and Grove (1985) reported a $Kd_{Cr(VI)}$ of 52 L/kg at a pH of 6.8 for alluvial sands. Sandy material has a greater preponderance of positively charged surfaces over the pH 5 – 7.5 range, compared to clay (isoelectric point pH of 2 - 3.5). This resulted in greater affinity for CrO_4^{2-} and a correspondingly higher $Kd_{Cr(VI)}$ for sand compared to clay. Davis and Olsen (1995) compiled published data on Cr(VI) sorption, demonstrating the effect of pH and soil type on $Kd_{Cr(VI)}$, and observed a linear relationship between Kd and the pH for sands and clays (Fig. 2.5).

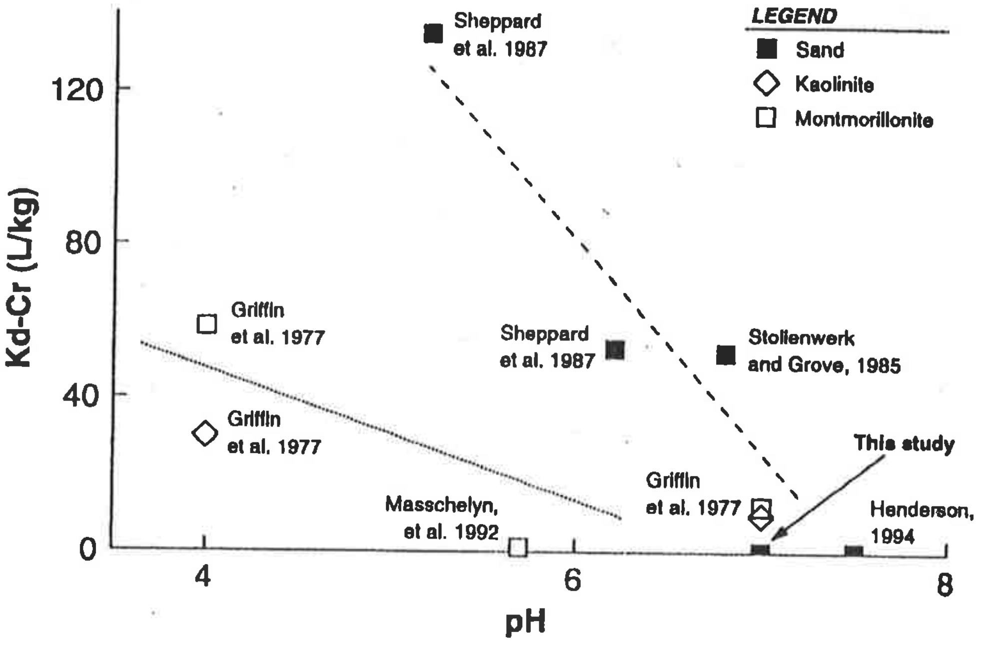

Fig. 2.5 Sorption data demonstrating the effect of pH and soil type on $Kd_{Cr(VI)}$ Sand (dashed line) and clays (dotted line) (Source: Davis and Olsen, 1995)

James (1994) studied Cr(VI) leaching behaviour in chromite ore processing residue contaminated soils by extracting them with distilled water, 1.0 mM KNO_3 in 0.5 mM K_2SO_4 (salt solution, pH 7) and 1.0 mM HNO_3 in 0.5 mM H_2SO_4 (acid solution, pH 2.7). He observed no difference between distilled water, salt solution and dilute acid in the extraction of Cr(VI) from two soils. Despite the fact that the repeated leachings of the soil with acid gradually lowered the pH of the extracts, Cr(VI) concentrations were unchanged from water and salt solutions. He attributed this to the presence of a solid phase containing sparingly soluble Cr(VI) for a gradual and steady release of Cr(VI) from the contaminated soils. Depending on the source of chromate contamination and the nature of adsorbed phase, at times the solubility of Cr(VI) could be independent of soil solution pH.

Studies in our laboratory demonstrated a similar gradual and steady leaching of Cr(VI) from surface alkaline soil contaminated with tannery waste at Mount Barker, South Australia (Naidu et al., 2000b; Kookana et al., 2000; Avudainayagam et al., 2001).

2.2.14.2 Adsorption of Cr(VI)

Adsorption of Cr(VI) by soils and standard minerals has been studied extensively. Modeling efforts of Cr(VI) sorption on hydrous oxides of Fe and Al and in soils suggest that Cr(VI) forms an outer-sphere complex on these surfaces (Benjamin and Bloom, 1981; Zachara et al., 1987, 1989; Ainsworth et al., 1989). In contrast to results of surface complexation modeling, competitive ion displacement studies have shown that Cr(VI) is retained much more strongly than anions such as Cl^- or SO_4^{2-} and that the retention strength approaches that of phosphate (Bartlett and Kimble, 1976b; Griffin et al., 1977). To ascertain definitely whether Cr(VI) forms an inner sphere or outer sphere complex, Fendorf (1995) employed XAFS (X-ray Absorption Fluorescence Spectroscopy) to identify the Cr(VI) surface complex on Al and Fe hydrous oxide. He found that Cr(VI) formed an inner-sphere complex on goethite, with both bidentate and monodentate complexes (Fig. 2.6). Based on these results one would therefore expect that Cr(VI) also forms an inner-sphere complex on Al hydrous oxides. However, Aide and Cummings (1997) proposed an outer sphere complex of Cr(VI) adsorption on Al-oxyhydroxide (boehmite). They demonstrated that Cr(VI) adsorption on boehmite is pH dependent and this pH dependency is strongly related to the protonation of CrO_4^{2-} to form $HCrO_4^-$. They also observed suppression of Cr(VI) adsorption by dilute concentrations of o-phosphate competing for similar substrate sites.

Therefore it is possible that both specific and non-specific adsorption of Cr(VI) can be observed in soils and pH and soil solution composition may have greater influence on the solubility and mobility of Cr(VI) in soils.

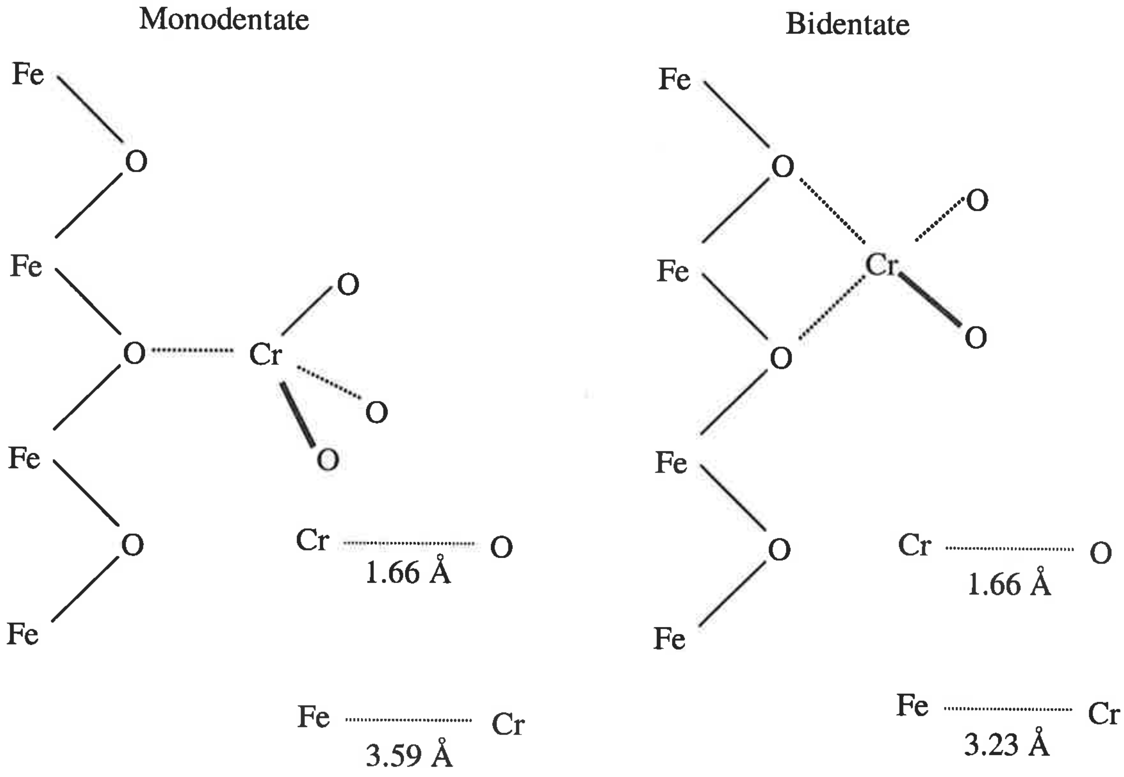

Fig. 2.6 Surface complexation structure of Cr(VI) on goethite. Note the interatomic distances and atom types coordinating Cr(VI) (Source: Fendorf, 1995)

2.2.15 Contaminated Soil Environment and Mobility of Cr(VI)

Essentially the contaminated soil environment would depend on the source of contamination, namely dumping of industrial solid or liquid wastes. The nature and composition of the waste would determine the solubility and precipitation of Cr(VI) disposed along with the waste to soil. The tanning industry generates approximately 50,000 tons of solid waste per year from chromium mediated tanning in India and surrounding countries (Ramasamy and Naidu, 2000), while in the United States, tanneries generate between 80,000 to 100000 (wet) tons of sludge annually (Ho et al., 1982).

2.2.15.1 Tannery Sludge Composition

Chrome tanning produces two types of sludge, hair-burn and chrome. The hair-burn or de-hairing sludge results from the initial stages of the process, when salt-cured hides are mechanically scraped and soaked in $Ca(OH)_2$ to remove hair. The residual sludge contains high concentrations of organic carbon, total N, Ca^{2+}, Mg^{2+} and Na^{+}, but relatively small amounts of Cr. After de-hairing, the hides are cleaned and soaked in a $NaCl\text{-}H_2SO_4$ solution, then bathed for several hours in a basic $Cr(SO_4)_3$ tanning solution. The hides are then neutralized with $NaHCO_3$. This last stage yields the chrome sludge, with high Cr concentration along with high concentrations of organic carbon, total N, Ca^{2+}, Mg^{2+} and Na^{+} (Dreiss, 1986). However, the composition of sludge varies from place-to-place and industry-to-industry and depends upon the choice of chemicals, raw materials, pre-treatment methods employed for the waste water and above all the quality of water used for the tanning processes. For a comparison, the tannery sludge composition data reported for India, South Australia and the United states are presented in Table 2.3.

Table 2.3 Chemical composition of tannery chrome sludge from different countries

Composition of tannery sludge	South Australia[1]	USA[2]	South India[3]
pH	7.71	*	7.8
EC (dS m^{-1})	3.5	*	3.5
Total organic carbon (%)	11	15.4	9.6
Cr (%)	0.08	3.04	3.86
$CaCO_3$ (%)	11.7	*	*
Ca (%)	0.8	4.7	1.8
Na (%)	*	4.7	0.7
Fe (mg kg^{-1})	1.1	*	*
Mn (mg kg^{-1})	1.3	*	*
Cu (mg kg^{-1})	66.5	*	*
N (mg kg^{-1})	*	31000	4300
P (mg kg^{-1})	4032	*	5100
K (mg kg^{-1})	3549	1900	40

* Not reported; [1] (Naidu et al., 2000c); [2] (Lollar , 1955); [3] (Sara Parwin Banu et al., 2000)

2.2.15.2 Soil Solution Composition and Mobility of Cr(VI)

In terms of ionic activity and solubility of Cr(VI) in soil solution, the presence of high concentrations of Ca^{2+}, Na^{+}, PO_4^{3-} and SO_4^{2-} in tannery contaminated soils has a significant influence on the mobility of Cr(VI) in such soils. James and Bartlett (1983c) studied the effect of sulphate and phosphate on the adsorption of Cr(VI) to two A and two B horizon soils and found that phosphate had a greater effect than sulphate in decreasing Cr(VI) adsorption by the soils. Aoki and Munemori (1982) showed that adsorption of chromate by iron oxide was increased in the presence of cadmium, lead, copper and zinc divalent cations. Zachara et al., (1987) studied the chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. They found that in paired-solute systems (e.g., CrO_4^{2-}-H_2CO_3), anionic co-solutes markedly reduce CrO_4^{2-} adsorption through a combination of competitive and electrostatic effects, but observed no appreciable influence of cations (K^+, Mg^{2+} and Ca^{2+}). However, studies on the effect of dominant cations and anions present in the tannery waste on Cr(VI) mobility in a contaminated soil is lacking. Hence, in the present study this was included as one of the objectives.

2.2.16 Remediation of Chromate Contaminated Soil and Water

There are a number of treatment technologies available for soils which are contaminated with high levels of Cr(VI) other than conventional remediation by excavation and off-site disposal. As with soils, a wide array of treatment technologies is available to remove chromate from water. However, the selection and application of the type of treatment technology would depend upon many physical and chemical factors of the soil and water at the contaminated site.

2.2.16.1 Remediation Strategies for Contaminated Soil

The technologies applicable to a particular Cr site depend on the cleanup goals, the forms of Cr present and the volume and physical/chemical properties of the Cr-containing soils. Cr(III) does not pose a significant groundwater or surface runoff hazard. In contrast, Cr(VI) is highly mobile in the soil and water environment, is acutely toxic at moderate doses and classified as known respiratory carcinogen in humans (USEPA, 1996a).

Most of the developed countries have proposed distinctly different risk-based criteria for Cr(III) and Cr(VI) in soils. The threshold levels of both the forms of Cr permissible in soils recommended by some developed countries are listed in Table 2.4.

Region III of the U.S. Environmental Protection Agency (USEPA) has established a risk based residential soil cleanup level of Cr(III) of 78,000 mg/kg and Cr(VI) of 390 mg/kg based on an ingestion pathway (USEPA, 1996b). The United States Environmental Protection Agency has also designated a soil screening level of 270 mg/kg Cr(VI) for potential human exposure by inhalation (USEPA, 1996c). The National Environmental Protection Council of Australia (NEPC, 1999) is currently developing a new soil investigation level for various contaminants including both Cr(VI) and Cr(III). The new soil investigation levels of Cr are categorized into health investigation and ecological investigation levels.

Table 2.4. Threshold levels of Cr(III) and Cr(VI) permissible in soils of some developed countries (mg/kg)

Australia[a]	New Zealand[b]	UK[c]	Canada[d]	USEPA[e]	Germany[f]
50[1]	600[2]	600[2]	250[2]	1500[2]	200[2]
	10[3]	25[3]	8[3]	-	-

[a] ANZECC/NHMRC (1992), [b] Ministry of Environment/Ministry of Health (1995), [c] UK Department of Environment (1987); [d] CCME (1990); [e] USEPA (1993); [f] Marshall (1994).

[1] Total Cr, [2] Cr(III), [3]Cr(VI)

Another cleanup criterion often used for sites is the Toxicity Characteristic leaching Procedure (TCLP) and the limit for total Cr is 5 mg/L (40 CFR 261.24, as quoted by Higgins et al., 1997). This procedure measures leachable Cr concentrations which is predominantly Cr(VI) and may be followed in the United States. So in terms of setting cleanup standards for Cr, the highly mobile and toxic Cr(VI) is given more importance than the immobile Cr(III) in soil and water environments.

2.2.16.2 Soil Remediation Technologies

Apart from removing the Cr(VI)-containing soils from a site, other available technologies consists of (1) removing the Cr(VI) from the soil, (2) immobilizing the Cr so that it will not leach as defined by the TCLP test and (3) irreversibly reducing the Cr(VI) in the soil to the Cr(III) valence state. The list of treatment methods under each category, advantages and disadvantages are presented in Table 2.5.

Sites where the extent of contamination is large, in hectares, and the total Cr concentrations are high, *in-situ* treatment methods are the most suitable options. If a considerable amount of total Cr(VI) was observed then irreversible reduction of Cr(VI) to Cr(III) by using an appropriate reducing agent would be an effective and economical remediation approach. Above all, the proposed use of the land after decontamination has to be considered in selecting suitable *in-situ* treatment methods.

2.2.16.3 Irreversible Reduction of Cr(VI) to Cr(III)

From the literature it can be understood that extensive research has been directed towards the reduction of toxic and mobile Cr(VI) to relatively non toxic and immobile Cr(III) in soil and water (James and Bartlett, 1983c; Eary and Rai, 1988; Powell et al., 1995; Wittbrodt and Palmer, 1995, 1996a, 1996b; Fendorf and Li, 1996; Buerge and

Table 2.5 Remediation technologies for chromate contaminated soils

Technology	Advantage	Disadvantage
Removal of Cr (VI)		
Excavation and off-site disposal	Appropriate for small volumes of soil, quick to implement, uses readily available equipment, completely removes Cr	May cause Cr(VI) to become airborne and health hazard, may invoke land disposal restrictions, can be expensive especially for deep material, soil may need treatment, adding to the cost
Soil washing	May greatly reduce the volume of contaminated material that requires treatment	May cause Cr(VI) to become airborne and health hazard during excavation, Cr is transferred from soil to water source, not appropriate for soils with strongly bound Cr(VI)
Soil flushing	In-site technology, does not require excavation. Demonstrated technology for remediating Cr(VI) spills (McPhillips et al., 1991)	Generates contaminated water, not appropriate for soils with strongly bound Cr(VI)
Immobilization of Cr(Vi)		
Solidification/stabilization Ex-situ	Relatively inexpensive Demonstrated technology (USEPA, 1989)	May cause Cr(VI) to become airborne and health hazard during excavation, does not destroy contaminants, generates increased volume of solidified mass that requires disposal, Cr(VI) may need to be reduced to Cr(III), not appropriate for sites where total Cr levels must be decreased, may require soils dewatering
Solidification/stabilization	In-situ technology, does not require excavation. Applicable to sites with high water table	Cr(VI) may first need to be reduced to Cr(III), not appropriate for sites where total Cr levels must be reduced
Vitrification	May be performed in-situ Reduce and immobilize Cr(VI) May produce marketable byproduct	High energy requirements, may require soil de-watering, may require significant amounts of additives
Reduction of Cr(VI) to Cr(III)		
Chemical reduction	May be performed in-situ Applicable to beneath buildings and other substances	Not appropriate for sites where total Cr levels must be decreased, other compounds in soil may consume reducing chemicals and so process may require significant amounts of reducing agents
Biological reduction	In-situ technology, does not require excavation, applicable to sites with high water table Applicable to sites where Cr(VI) continues to leach from soil Applicable to beneath buildings and other structures	Not appropriate for sites where total Cr levels must be decreased, requires control of pH, oxygen, nutrients, etc. Process may be slow to achieve Cr(VI) reduction

Hug, 1997; Blowes et al., 1997; Patterson and Fendorf, 1997; Pettine et al., 1994; Seaman et al., 1999). Hexavalent Cr can be reduced to Cr(III) in soils by redox reactions with aqueous inorganic species, electron transfers at mineral surfaces, reaction with nonhumic organic substances such as carbohydrates and proteins, or reduction by soil humic substances (Palmer and Wittbrodt, 1991). However, the selection of suitable reducing agent is a prerequisite in achieving irreversible reduction of Cr(VI) to Cr(III) in contaminated soils. The irreversible reduction of Cr(VI) to Cr(III) is essential because of the possibility of re-oxidation of Cr(III) back to Cr(VI) by manganese oxides under favourable soil conditions.

Several effective Cr(VI) reducing agents have been tried; including ferrous iron (Eary and Rai, 1988), sulphide (Pettine et al., 1994), and organic complexes (Deng and Stone, 1996; Elovitz and Fish, 1995; Lay and Levina, 1996). Additionally, direct enzymatic reduction of chromate has been demonstrated by a number of soil microorganisms (Llovera et al., 1993; Ishibashi et al., 1990). Bartlett and James (1976b) found that soils high in organic matter reduced Cr(VI) to Cr(III) rapidly over a pH range of 4.4 - 7.6. However, James and Bartlett (1983b) demonstrated that Cr(III) form soluble chelated complexes with organic reductants and observed that even the organically complexed Cr(III) can be oxidizesd to Cr(VI) in soils.

It has been demonstrated that aqueous ferrous iron and sulphide can effectively reduce Cr(VI) to Cr(III) (USEPA, 1980; Pettine et al., 1994; Eary and Rai, 1988). The reduction of Cr(VI) to Cr(III) by ferrous iron is very rapid and is described by the following general equation:

$$\mathrm{Cr(VI)\ (aq) + 3Fe(II)\ (aq) \Leftrightarrow Cr(III)\ (aq) + 3Fe(II)\ (aq)} \text{ ------------------- } (1)$$

Eary and Rai (1988) studied the reduction of aqueous Cr(VI) by Fe(II) and observed that the products of the reduction reaction (1) precipitates as hydroxide solids in slightly acidic to alkaline solutions depending on the solution concentrations, i.e.

$$_{x}Cr(III) + (1\text{-}x)Fe(III) + 3H_2O \Leftrightarrow (Cr_xFe_{1-x})\ (OH)_3(s) + 3H$$

Where x can vary between 0 and 1. Cr(III) hydroxide solids, including $Cr(OH)_3(s)$ and the solid solution $(Cr,Fe)(OH)_3(s)$, have been observed to precipitate rapidly in moderately acidic to alkaline solutions and are expected to be important solubility-controlling solids for dissolved Cr(III) over a wide range of pH (Rai et al., 1987; Sass and Rai, 1987). Further to the precipitation they observed that the solubility of this solid limits Cr(III) concentrations over the pH range of approximately 5 - 11 to less than the drinking water standard of 0.05 mg/L of Cr.

Therefore, based on the published reports on aqueous Cr(VI) reduction by reducing agents, it is obvious that use of ferrous iron may be the best option to achieve irreversible reduction of Cr(VI) to Cr(III). However, very limited studies are found in the literature reporting the use of ferrous iron for reducing Cr(VI) to Cr(III) in soil and especially in contaminated soils.

James (1994) studied the reduction of water soluble and exchangeable Cr(VI) in alkaline soils enriched with chromite ore processing residue using various reducing agents including the ferrous iron. He observed that compared to Mn^{2+}, steel wool, dried hard wood tree leaf litter, ferrous iron reduced all of the soluble and exchangeable Cr(VI) in the soils. However, he also noted that ferrous iron acidified the soil more than the Mn^{2+} treatments. Seaman et al., (1999) studied in-situ reduction of Cr(VI) within coarse textured, oxide coated soil and aquifer system using Fe(II) solutions. He found a decrease in the concentrations of Cr(VI) in the batch and column effluent with increasing Fe(II). However, dissolved Cr, presumably Cr(III), exceeded regulatory limits due to the low pH (3.0) induced by oxidation and hydrolysis of Fe(II).

There are no published reports on Cr(VI) reduction in tannery waste contaminated soils and no studies on re-oxidation of reduced Cr(III). Therefore in the present study water soluble and exchangeable Cr(VI) reduction in the tannery waste contaminated soil was investigated using Fe(II) as the reducing agent as well as the re-oxidation of reduced Cr(III) by conducting prolonged incubation experiments.

2.2.17 Remediation of Cr(VI) Contaminated Water

Chromium is used in a number of industries that generate large volumes of Cr(VI)-contaminated wastewater. Among the Cr use industries, some may be generating wastewater containing Cr(VI) as the dissolved Cr species, namely Cr plating and chemical milling and etching industries (USEPA, 1979).

Apart from the generation of large volume of Cr(VI) dissolved industrial waste water, indiscriminate disposal of Cr rich wastewater to land have resulted in contamination of groundwater with Cr(VI). The groundwater contamination of Cr(VI) is more commonly observed in industrialized areas in the developing part of the world. Large plumes of Cr(VI)-contaminated groundwater in shallow sand and gravel aquifers have been well documented (Deutsch, 1972; French et al., 1985; Perlmutter and Lieber, 1970; Stollenwerek and Grove, 1985; Wiley, 1983). Disposal of tannery effluent and sludge onto the land has resulted in severe contamination of soil and groundwater quality by Cr in Vellore district of Tamil Nadu, India (Mahimairaja et al., 2000).

Therefore, to safeguard the dwindling natural resources, it is necessary to treat the contaminated groundwater and industrial wastewater to remove toxic Cr(VI).

2.2.17.1 Water Treatment Methods to Remove Cr(VI)

Chemical precipitation is the most common technique followed for the removal of heavy metals from wastewater. The chemicals most frequently used for precipitation of metals are lime, caustic and sodium carbonate. Although most of the heavy metals are precipitated readily by pH adjustment, Cr(VI) is highly soluble and does not precipitate from solution at any pH. Consequently, treatment for Cr(VI) usually consists of a two stage process: firstly, the reduction of Cr(VI) to Cr(III) and, secondly, the precipitation of Cr(III). Reducing agents commonly employed are gaseous sulphur dioxide or a solution of sodium bisulphate (Lanouette, 1977). Other suitable reducing agents include sodium sulphite, sodium hydrosulphite and ferrous sulphite (Kraljik, 1975). However, there are no published reports available on direct removal of Cr(VI) from water.

Recently, Tokunaga et al., (1999) demonstrated that lanthanum (La) salts can effectively remove As(III) and As(V) from contaminated waters. They showed that La was effective over a wide range of pH and demonstrated its ability to remove As to meet effluent and drinking water standards with a much smaller dose of La than would be required using conventional precipitants. Hexavalent Cr being an oxy-anion like As could behave similarly and precipitate from water as lanthanum salts. With this hypothesis, in the present study, a La salt was tried evaluated for it's ability to to precipitate Cr(VI) from water.

2.2.18 Summary

From the published literature it is known that extensive research has been carried out investigating speciation of Cr in soil, effect of pH on soil solution concentration of Cr(III) and Cr(VI), soil adsorption phenomena of Cr species, redox reactions and transformation of Cr(III) to Cr(VI) and vice-versa and certain remediation strategies to decontaminate Cr contaminated soils. Most of the studies were conducted in normal soils spiked with Cr and very limited research was conducted using contaminated soils. Furthermore, studies on tannery waste contaminated soils can be numbered and obviously a gap in knowledge exists in understanding the influence of long-term tannery waste contamination on Cr behaviour in soil. Therefore in the present study following specific objectives were addressed;

- Investigate the effect of electrolytes, namely, Ca^{2+}, Na^{+} and PO_4^{3-} the dominant cations and anion commonly found in tannery contaminated soils on the mobility of Cr from surface and sub-surface soil;
- Study the influence of long-term contamination (aging) on the nature of Cr species by solid phase speciation of Cr partitioned to various soil components for the surface and subsurface soil of the contaminated site;
- Study the efficiency of ferrous sulphate as an *in-situ* chemical reductant to irreversibly reduce Cr(VI) in the contaminated surface soil under various experimental conditions; and
- Investigate the potential use of lanthanum (La^{3+}) to completely remove Cr(VI) from water.

CHAPTER 3

General Materials and Methods

3.1 Study Site

The present study was based at the tannery waste contaminated site at Mount Barker, South Australia (Plate 3.1). This site was used for tannery effluent and waste disposal until early 1980, when the tannery industry closed its operation and donated the land to the Mount Barker City Council. Given that contamination at the site ranges from 0.1 to 62 g/kg, the site was declared contaminated following implementation of regulatory measures during the early 1980's. Subsequently, sections of the contaminated site were bulldozed and vegetated with trees. The Cr concentrations of the subsurface soils at this site often exceed 1000 mg/kg. Given the strongly duplex (sandy surface and clayey subsurface horizons) nature of the soils at this site, there appears to be appreciable lateral movement of Cr in subsurface water samples (Naidu et al., 2000b).

3.1.1 Soils

As the major objective of the present study was to investigate the factors that control chemo-dynamics of Cr at the site, surface (0 to 15 cm) and subsurface soil samples were collected from sites highly contaminated with tannery waste. This was achieved by digging a soil pit of 120 x 120 x 100 cm size at the site where the highest level of total Cr contamination was reported (Naidu et al., 2000b). In the vertical soil profile three distinct

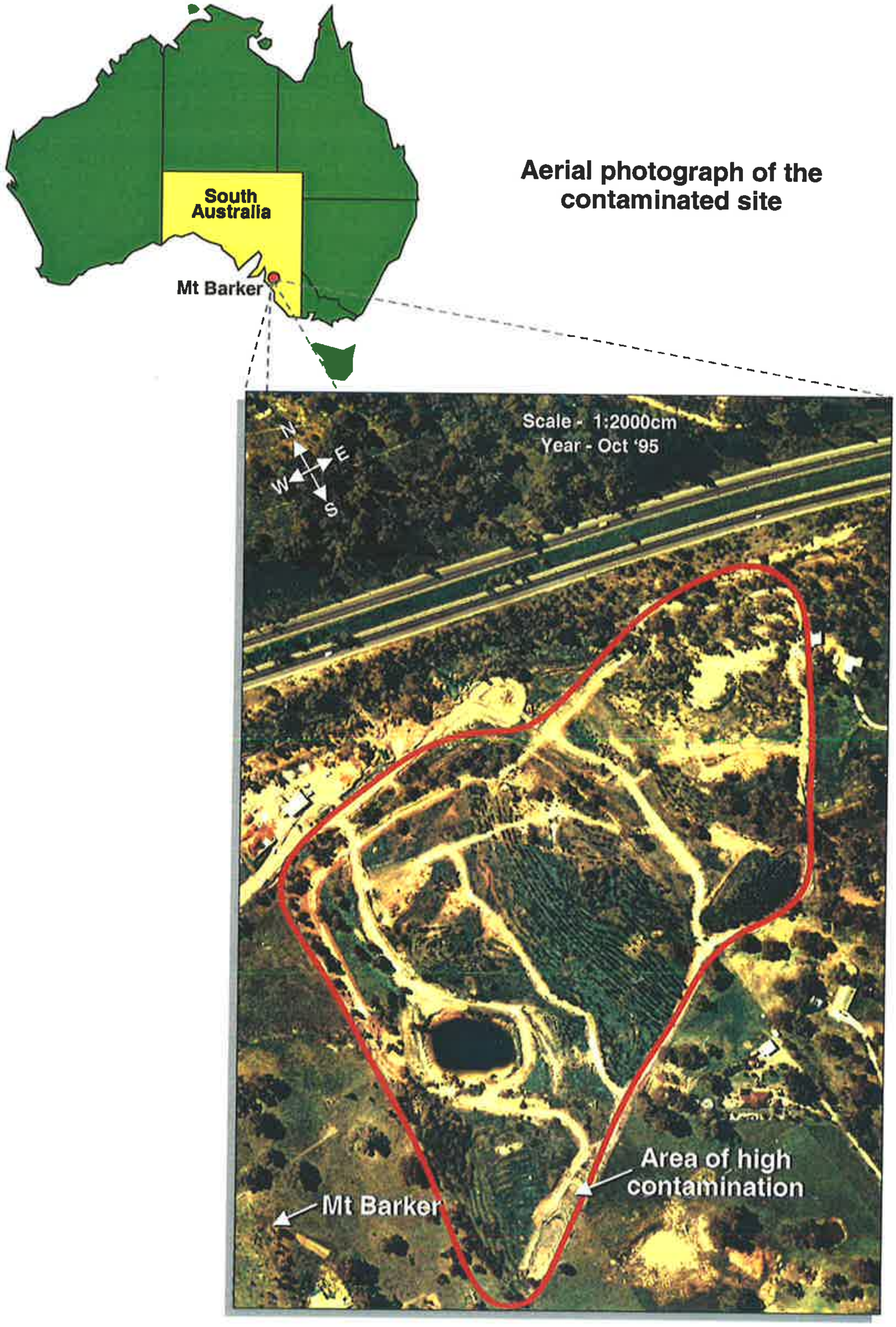

Plate 3.1. Aerial photograph showing the contaminated site at Mount Barker, Adelaide, South Australia.

horizons were present viz. 0 – 15 cm green coloured sludge mixed with soil, 15 – 50 cm loamy sand and at > 50 cm clay rich soil. Chromium contamination at the site ranged from 300 to 60000 mg/kg. From soil core analysis in earlier studies decreasing Cr concentration with depth had been observed. Therefore, soil samples were collected from three horizons starting from the base upward to minimize contamination. The samples were collected in large polyethylene bags for transportation to the laboratory. After drying in a fan-forced oven at 40°C, samples were crushed to pass through a 2-mm stainless steel sieve and stored in airtight polyethylene containers for use in all experiments.

3.2 General Analytical Procedures

3.2.1 Routine Analysis

The soil collected from each horizon of the profile was characterized for physical and chemical properties using standard methods. Soil pH and EC (Electrical Conductivity) were measured in 1:5 (w/v) soil-water suspensions following end-over-end equilibration for 1 h and total carbon (TC) was estimated by dry combustion in a LECO CR12 analyser (Rayment and Higginson (1992). Chromium and other metal concentrations in soils were measured following aqua-regia digest of the soils over a hot plate at 110 °C (Merry and Zarcinas, 1980).

3.2.2 Speciation of Cr – Capillary Zone Electrophoresis

Aqueous speciation of Cr is critical because even in trace concentrations (0.05 mg/L) Cr(VI) is toxic. Therefore, greater attention was given to speciation of Cr in environmental samples. A number of instrumental techniques have been used to speciate

Cr in the environment including ion chromatography (IC), high performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) (Thompson and Houk, 1986; Beauchemin et al., 1988) and IC coupled with ICP-MS (Sheppard and Thibault, 1992). Another method successfully used is cathodic stripping voltametry (van den Berg and Khan, 1990; Zelic and Branica, 1990). However, most of these methods are either difficult to perform, subject to interferences, or require expensive equipment. Capillary zone electrophoresis (CZE) is a highly versatile analytical technique that is increasingly being used to speciate a wide variety of inorganic and organic species (Hodgson et al., 1988; Haddad and Jackson, 1990; Jackson and Haddad, 1993; Naidu, 1996; Naidu et al., 1997). This emerging technique allows for the rapid separation of charged compounds on the basis of differences in their electrophoretic mobilities. The more established technique of IC uses large volumes of mobile phase and requires a reasonably large sample size. In comparison, CZE uses ultra low volumes of electrolyte, typically achieves separations in < 5 to 10 min, requires only nL of sample and the running costs are low. Given that new methods that are sensitive and cost effective, if developed, could potentially be established in the environmental research laboratory in India, we decided to assess the potential for using capillary electrophoresis to speciate Cr in soil water extracts.

In our laboratory we developed a simple method for the simultaneous determination of Cr(III) and Cr(VI) by capillary zone electrophoresis (CZE), where Cr (III) was chelated with ligands to form anionic complexes. Nitrilotriacetic acid (NTA), N-2-hydroxyethylethlendiaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), and 2,6-pyridinedicarboxylic acid (PDCA) were investigated as Cr (III) complexing ligands.

3.2.2.1 Experimental Section

3.2.2.1.1 Chemicals

All reagents (analytical grade) were obtained from Sigma and Aldrich (Sydney, Australia) and dissolved in Milli-Q water without further purification. Standard solutions of $K_2Cr_2O_7$ and $CrCl_3.6H_2O$ were prepared daily from a 10 mM stock solution in Milli-Q water and diluted to the required concentrations before use. Electrolytes required for CZE were prepared by dissolution of an appropriate amount of NaH_2PO_4 in Milli-Q water, which contained appropriate amounts of tetradecyltrimethylammonium bromide (TTAB) and organic solvent. All electrolytes were filtered through a Millipore 0.45 μm membrane filter and degassed in an ultrasonic bath prior to use. Electrolyte pH was adjusted with 0.1 M NaOH or 0.1 M H_3PO_4 solution.

3.2.2.1.2 Sample Preparation

An excess of ligand, 4 mM ligand (1.0 ml), was added to a test tube containing 1 mM $CrCl_3.6H_2O$ (0.5 ml) and heated on a water bath for 5 mins at 80 ^{0}C. Heating is required because Cr(III) is kinetically inert. After cooling to room temperature, the mixture was subjected to CE analysis (Timerbaev et al., 1996b). Soil solution was obtained by extracting the contaminated soil with water at 1:5 ratio (soil: Deionised) for 2 h in an end over end shaker, centrifuged at 32570 g for 15 min and filtering through 0.45 µm Schleicher and Schuell syringe filters. Total Cr and soluble Cr(VI) in the soil solution was analysed on the same day.

3.2.2.1.3 Instrumentation

All CZE experiments were preformed using a Quanta 4000 instrument (Waters, Milford, USA). The system was controlled by Millennium (Waters, Milford, USA) software. Separation was carried out on fused-silica capillaries with 80 cm (~~75.5 cm x~~ 50 μm I.D., 75.5 cm effective length). The UV detector was set at 185 or 214 nm. Total Cr was determined using AAS (GBC, Model 906, Australia). Cr(VI) was analysed by ion chromatography using standard method 7199 (USEPA, 1996).

3.2.2.1.4 Electrophoretic Procedures

Prior to use, a capillary was pretreated with the following cycles: 0.1 M NaOH for 20 min, 0.01 M NaOH for 20 min, deionized water for 30 min and 30 mM phosphate buffer for 30 min. The capillary was pre-conditioned with phosphate buffer for 2 min before each run. Samples were injected in the hydrostatic mode for 30 s. The capillary was held at 25 ^{0}C, and the applied constant voltage was -20 kV. Identification of each of the solutes was based on the migration time and was verified by spiking samples with known standards. 0.05% (v/v) benzyl alcohol was used as a neutral marker for the determination of the electrophoretic mobility. The electroosmotic mobility and the electrophoretic mobility of the solute and marker were calculated using equations described previously.

3.2.2.2 Results and Discussion

3.2.2.2.1 Choice of Complexing Ligand for Cr(III)

In order to achieve high UV response and selectivity, complexing ligands should satisfy several requirements including (1) the ligand should only form a single distinct complex with Cr (III) under derivatization conditions; (2) the complex should remain stable during electrophoresis, and (3) the complex should have large UV absorptivity (~~Liu et al., 1999a;~~ Liu et al., 1998; Liu et al., 1999a,b). In this work, EDTA, HEDTA, DTPA, NTA and 2,6-PDCA were tested as ligands for chelation with Cr (III). The complexes formed were separated using an electrolyte containing 30 mM phosphate, 0.5 mM TTAB at pH 6.0 as shown in Fig. 3.1 (a-e). For all five ligands, the Cr(III) complexes were detected together with excess free ligand.

The free ligand peaks appeared before the Cr (III) anionic complex peaks because their charge/mass ratio was greater than that of the Cr(III) anionic complexes. However, two or more peaks of small UV response were observed using EDTA, HEDTA and DTPA. This can be attributed to the formation of different Cr(III) anionic complexes under the derivation conditions (Dabek-Zlotorzynska et al., 1998). In contrast, only one complex peak was observed using either 2,6-PDCA or NTA as a complexing ligand. However, a larger UV response for the Cr (III) complex was obtained using 2,6-PDCA due to the complexes larger absorptivity (43680 M^{-1} cm^{-1}, 192 nm) (Soga and Ross, 1997). However, in this study, there was less UV response for all 5 ligand complexes at 214 nm. This was not unexpected, since the carboxylate group of the ligand has stronger absorbency below 210 nm (Semenova et al., 1996; Timerbaev et al., 1996b; Pozdniakova and Padarauskas, 1998). For example, Cr (III) chelated with 2,6-PDCA at 185 nm had a peak area 6 times greater than that obtained at 214 nm. The selectivity of the ligand for common metal ions (Ca(II), Mg(II), Mn(II) , Zn(II), Co(II), Cd (II), Ni(II), Cu(II), Pb(II), Fe(III)) was also tested. This indicated that EDTA, HEDTA and DTPA chelated with most of the tested metal ions, while NTA and 2,6-PDCA showed a higher specificity for Cr(III). Although 2,6-PDCA complexed with Ni(II), Cu(II) and Pb(II) forming $[M(L)_2]^{2-}$(Haddad and Jackson, 1990), these complexes have significantly different mobilities to $[Cr\ (L)_2]^{1-}$ due to the lower charge and therefore does not interfere with the determination of Cr(III). Thus, 2,6-PDCA was the most suitable ligand for Cr (III) determination because it satisfied the above requirements most readily.

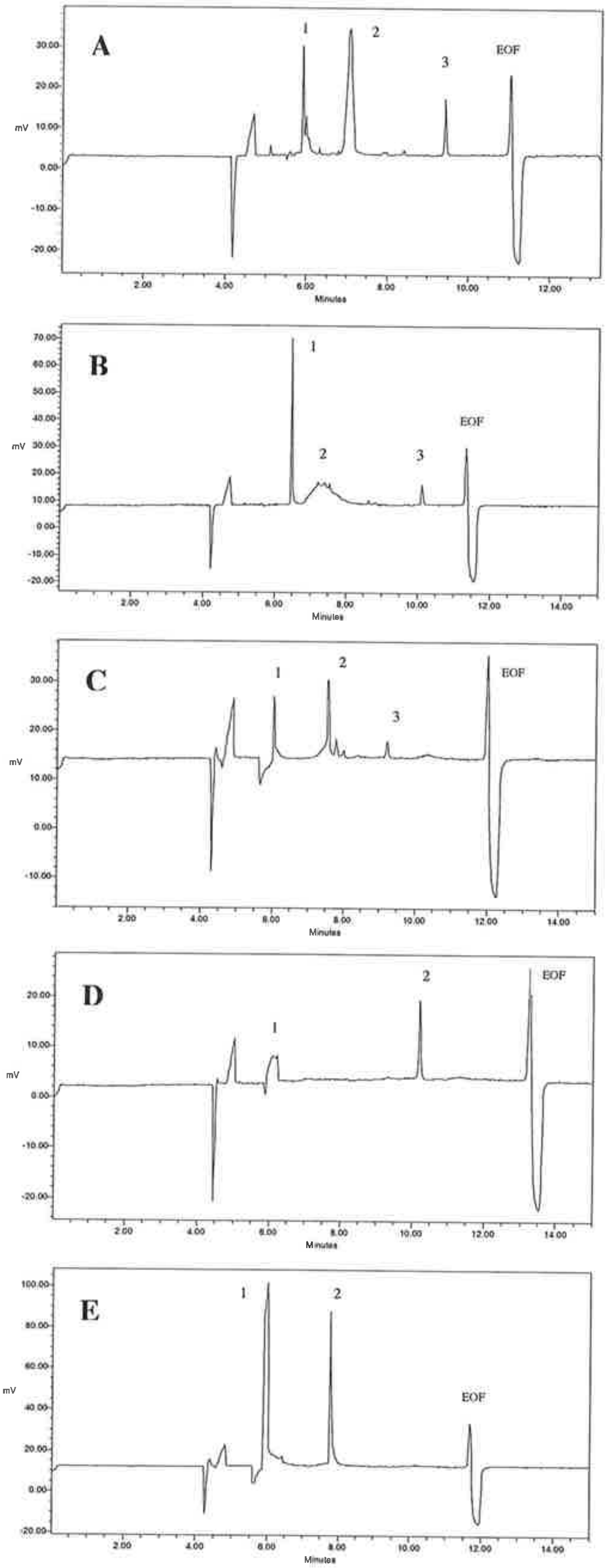

Fig. 3.1 Electropherograms of Cr(III) complexed with (a) EDTA.(b)HEDTA (c) DTPA (d) NTA and (e) 2,6-PDCA. 1. free ligand; 2. Cr(III)-complex (I); 3. Cr(III)-complex (II). Instrument and separation conditions: 0.25 mM Cr(III), fused-silica capillary 80 cm x 50 μm (effective length: 75.5 cm); electrolyte, 25 mM sodium phosphate, 0.25 mM TTAB, 15 % (v/v) acetonitrile at pH of 6.40; applied potential, -20 kV; hydrostatic injection: 30 s, UV detection at 185 nm. Capillary temperature, 25 ^{o}C.

3.2.2.2.2 Pre-column Derivitization Conditions

Previous work using 2,6-PDCA as an eluent in ion chromatography (Janvion et al., 1995; Ding et al., 2000) has shown that eluent pH and ligand concentration play important roles in the formation of anionic complexes. Similarly, the conversion of Cr(III) to an anionic Cr(III) complex is highly dependent upon on pH and the concentration as shown by the following equations (Haddad and Jackson, 1990).

$$Cr^{3+} + 2PDCA^{2-} \Leftrightarrow [Cr(PDCA)_2]^- \qquad (3.1)$$

$$H_2PDCA \Leftrightarrow 2PDCA^{2-} + 2H^+ \qquad (3.2)$$

$$Cr(OH)_3 \Leftrightarrow Cr^{3+} + 3OH^- \qquad (3.3)$$

Since the pKa values for 2,6-PDCA are pKa_1 2.16, and pKa_2 6.92, the effect of pH on the chelation reaction was tested in the range of 2.5 - 7.5. The formation of $[Cr(PDCA)_2]^-$ was determined by co-CZE at 185 nm. Figure 3.2 shows that the formation of $[Cr(PDCA)_2]^-$ significantly depends on solution pH. Peak area increased as the pH increased from 2.5 to 3.5. This can be attributed to an increase in the concentration of $PDCA^{2-}$, leading to formation of $[Cr(PDCA)_2]^-$ via equation 3.1. In contrast, peak area decreased when solution pH increased above 4.0. A higher solution pH leads to the hydrolysis of Cr(III) and to the formation of the precipitate described via equation (3.3). Therefore, the optimum solution pH of 3.5 was used in all subsequent experiments.

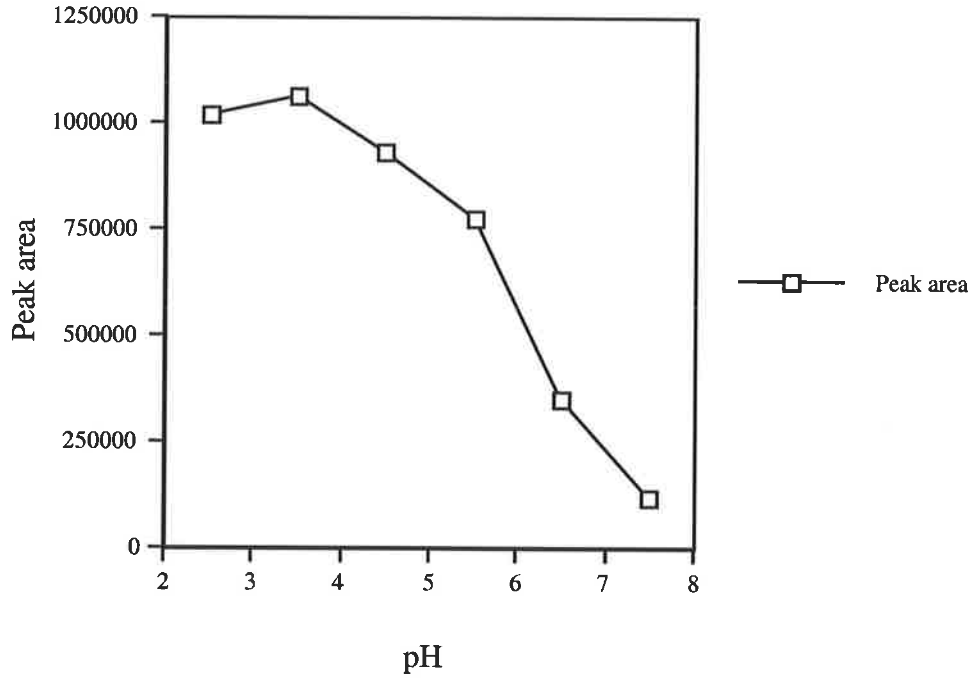

Fig. 3.2 Effect of pH on the chelating reaction between Cr(III) and 2,6-PDCA. 2,6 –PDCA: 1.0 mM; Cr(III): 0.25 mM. Instrument and separation conditions for similar to conditions used for Fig. 3.1.

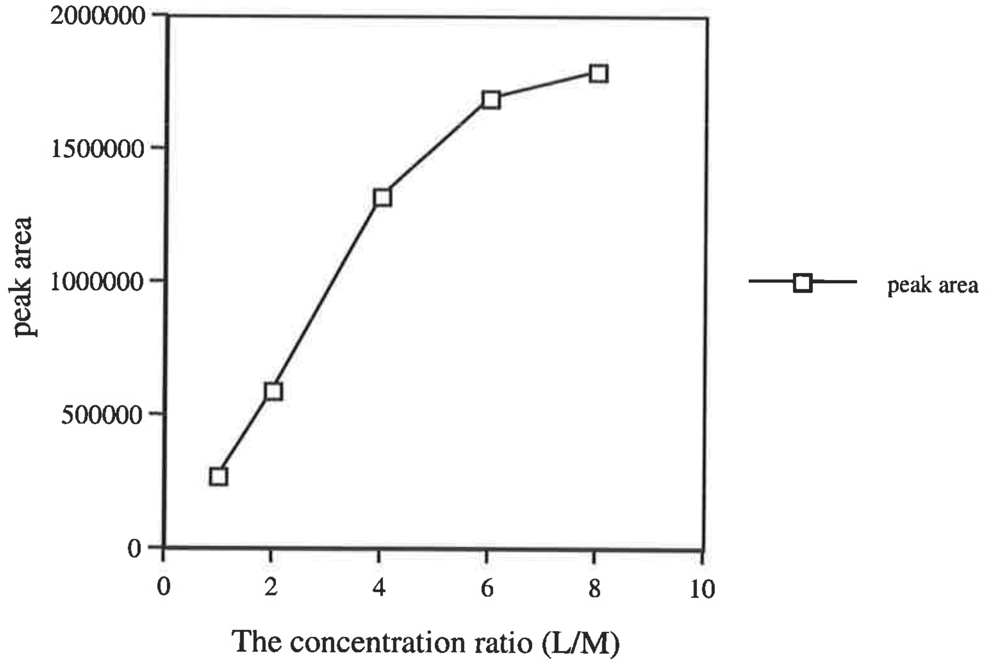

Fig. 3.3 Effect of the concentration ratio (L/M) on the derivitization. The solution pH: 3.5. Instrument and separation conditions for similar to conditions used for Fig. 3.1.

From equation (3.1), it can be seen that the concentration ratio (Cr (III)/ 2,6-PDCA) during derivatization affects the formation of $[Cr(PDCA)_2]^-$. The effect of the concentration ratio is shown in Figure 3.3. In general, peak area increased as the concentration ratio increased and peak area increased linearly up to a concentration ratio of 4. However, when ratio was above 6, the peak area was almost constant. At all concentration ratios only a single complex peak was observed. Similar results have been observed previously (Chen and Adams, 1999; Chen et al., 1999). A higher concentration ratio favors the forward chelating reaction because of the increasing of the concentration of 2,6-PDCA. Therefore, the best concentration ratio for obtaining maximum sensitivity was 6 [Cr(III): 2,6-PCDA].

The stability of $[Cr(PDCA)_2]^-$ was determined by repeated injection of solution derivatized at the concentration ratio of 6 at pH 3.5. The derivatization solution was then stored at room temperature and re-analysed daily. The solution exhibited excellent stability for up to 5 days (the response obtained from the sample at fifth day was 96.5% that obtained on the first day) at room temperature with no degradation being detected by CE. This indicates 2,6-PDCA was suitable for pre-column derivatization of Cr(III) with high selectivity.

3.2.2.2.3 Simultaneous Separation of Cr (III) and Cr (VI)

As shown in equations (3.1-3.3), there is a dynamic equilibrium between Cr (III), 2,6-PCDA and $[Cr(PDCA)_2]^-$. The equilibrium shifts during electrophoresis due to the dissociation of $[Cr(PDCA)_2]^-$. This problem can be overcome by the addition of small amounts of ligand to the running electrolyte (Liu et al., 1999a; Semenova et al., 1996; Timerbaev et al., 1996a; Jung et al., 1997; Pozdniakova and Padarauskas, 1998). In addition, the selectivity for the separation of metal anionic complexes can be controlled by the addition of organic solvent (Liu et al., 1999b). Thus, an electrolyte, containing 30 mM phosphate, 0.5 mM TTAB, 0.1 mM 2,6 –PDCA, and 15% acetonitrile at pH 6.4, was used as the running buffer for the separation of CrO_4^{2-} and $[Cr(PDCA)_2]^-$, and detected by direct UV at 185 nm. CrO_4^{2-} and $[Cr(PDCA)_2]^-$ were generally well separated with well defined peaks. Excess 2,6-PDCA was also detected, appearing prior to $[Cr(PDCA)_2]^-$ due to the ligands larger charge and smaller size. Some inorganic anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) commonly present in soils were added to the mixture of CrO_4^{2-} and $[Cr (PDCA)_2]^-$ to determinate whether they interfered with CrO_4^{2-} and $[Cr(PDCA)_2]^-$. Figure 3.4 clearly demonstrates that Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, CrO_4^{2-} and $[Cr(PDCA)_2]^-$ were all well resolved. The migration order was Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, $CrO_4^{2-}$and $[Cr(PDCA)_2]^-$. The migration order reflects differences in both charge and size of the solutes. For example, CrO_4^{2-} is double negatively charged and migrates faster than $[Cr(PDCA)_2]^-$ which is only single negatively charged.

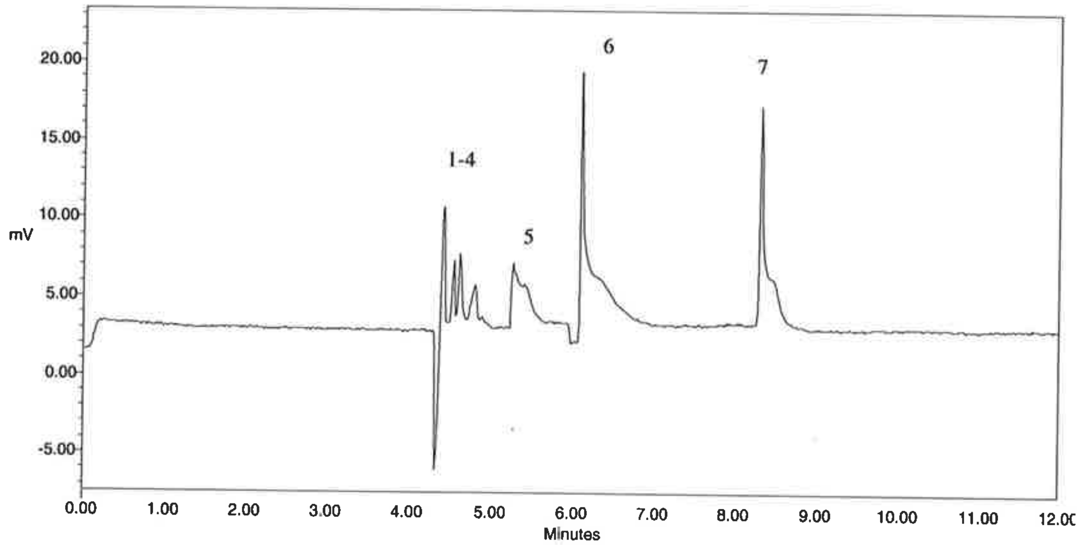

Fig. 3.4 Separation of Cr(III) and Cr(VI) under optimum CE conditions. 1. Cl^- (0.25 mM); 2. NO_2^- (0.25 mM); 3 NO_3^- (0.25 mM); 4. SO_4^{2-} (0.25 mM); 5. Cr(VI) (0.1 mM); 6. 2,6-PCD (0.25mM); 7. Cr(III)-complex (0.05 mM). Instrument and separation conditions: electrolyte: 30 mM sodium phosphate + 0.5 mM TTAB + 0.1 mM 2-6-PDCA+ 15.0% (v/v) acetronile at pH of 6.40 and other conditions as in Fig. 3.1.

Calibration plots were obtained by plotting peak area versus concentration. The relationship was linear in the concentration range 5-200 μM. Correlation coefficients (r^2) were in the range 0.9992-0.9999. The detection limits (S/N=3) were 2-3 μM and the reproducibility of the migration time (relative standard derivation, n=5) from injecting a 100 μM standard mixture was 0.7-2.4 %. Analytical characteristics of the test solutes using the proposed method are listed in Table 3.1.

The proposed method was used to determine Cr (III) and Cr (VI) in extracts of the contaminated soils. A typical electropherogram is presented in Figure 3.5(a). The contaminated soil contained only Cr(VI) in detectable concentrations. Peak assignment was verified by spiking the solution with a known concentration of Cr(VI) as shown in Figure 3.5(b). To confirm the proposed method for the determination of Cr(III), a known concentration of Cr(III) was also added to the soil. The determined concentrations using CZE are listed in Table 3.2, together with the concentration determined by spectrophotometry. The results obtained using the CZE technique showed good agreement with results obtained using spectrophotometry.

3.2.2.3 Conclusion

The results of this work demonstrated that 2,6-PDCA can be used as a derivatizing agent for Cr(III) and is therefore a useful ligand for the determination of chromium speciation when using CE with direct UV detection. The derivatization conditions, such as solution pH and the concentration ratio (M/L) are both important for the formation of a single stable $[Cr(PDCA)_2]^-$ complex. The proposed method offers high separation efficiency and short analysis time in comparison with conventional spectrophometric methods. However, it was found that the detection limits of CZE was higher (100 μg/L) than the detection limits of routine UV-VIS or Ion Chromatography methods (< 10μg/L) followed for the analysis of aqueous Cr(VI). Therefore, the more conventional methods described in the following section were adopted through out this study for the analysis of total Cr and Cr(VI) in soil solution.

Table 3.1 The characteristics for chromium species by the proposed method

Species	Regression line	Coefficient	Detection limit S/N =3 (μM)	Reproducibility (n=5, %)
Cr(III)	$y = 10\times10^5 x - 4.5\times10^3$	0.999	3	2.0
Cr(VI)	$y = 5.63\times10^5 x - 1.5\times10^3$	0.998	2	2.4

Table 3.2 The concentration of Cr (III) and Cr(VI) in contaminated samples determined by the CZE and UV methods

Species	CE (mg/l)	UV (mg/l)	spiked (mg/l)	found (mg/l)	Recovery CZE (n=3, %)
Cr(III)	-	-	2	1.96	98.0 ± 3.8
Cr(VI)	0.483	0.486	2	2.48	99.7 ± 2.9

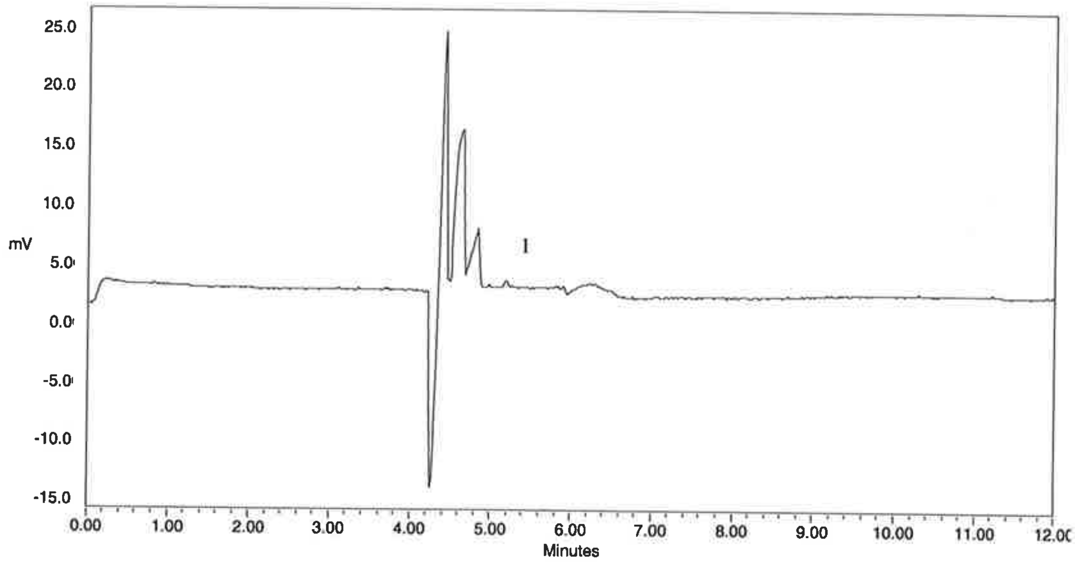

Fig. 3.5 (a) Contaminated soil extracts analysed by the proposed method. Soil extracts. 1. Cr(VI).

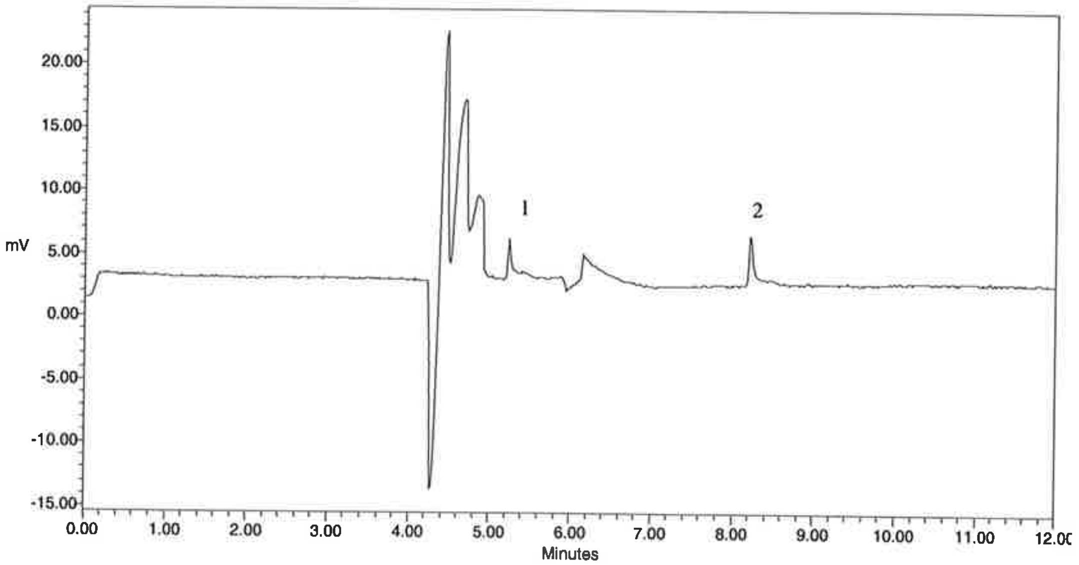

Fig. 3.5 (b) Contaminated soil extracts analysed by the proposed method. Soil extract spiked known Cr(VI) and Cr(III). 1. Cr(VI), 2. (Cr(III). Instrument and separation conditions were similar to those used for Fig. 3.4.

3.2.2 Speciation of Cr – Conventional Methods

Total Cr in solution was measured by flame atomic absorption spectrometry using the method described in APHA, 1992. Total soil Cr(VI) was measured following hot alkaline digestion (James et al., 1995). Solution Cr(VI) was measured by ion chromatography (DIONEX, Model 4000I, California, USA) using the Method 7199 developed by the U.S. EPA (USEPA, 1996) for the determination of Cr(VI) in drinking water, groundwater and industrial wastewater effluents. All analyses were conducted in duplicate and the mean values are presented in Table 3.3. The surface (0-15 cm) and subsurface horizons (15-50 cm) exhibited similar pH and soil physico-chemical characteristics. However, the pH and the chemical characteristics of the subsurface (50-90 cm) horizon were significantly different to those of the upper horizons and therefore detailed mineralogical analyses and further experiments were carried out on the surface (0-15 cm) and subsurface horizon (50-90cm). The soil was characterized as a silty loam for the surface (0 – 15 cm) and sandy clay for the subsurface (50 – 90 cm). The other selected properties of these two horizons are presented in Table 3.4.

Table 3.3 Selected characteristics of soils of the contaminated soil profile

Soil depth (cm)	pH 1:5 H_2O	EC (dS/m)	TC (g/kg)	Cr(VI) (mg/kg)	Fe^a (g/kg)	Mn^a (g/kg)	Cu^a (g/kg)	Cr^a (g/kg)
0-15	7.9	0.67	125	40.0	6.6	0.24	0.06	61.8
15-50	7.8	2.13	134	24.8	8.4	0.11	0.07	75.6
50-90	3.9	0.98	4.0	nd*	8.9	nd*	0.08	0.26

a - Aqua-regia extractable metals (g/kg)

3.2.3 Mineralogical Studies

Detailed mineralogical studies of whole soil samples were carried out by X-ray diffraction (XRD) using a Philips PW1800 microprocessor-controlled diffractometer. Characteristic X-ray diffraction patterns of surface and subsurface soil are presented in Figures 3.6 and 3.7. Quantitative analysis was performed on the XRD data using the commercial package SIROQUANT from Sietronics Pty Ltd. The background data was first subtracted and calibrated for the automatic divergence slit. A scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyser was used to investigate the nature of interactions between Cr and soil colloids. SEM was performed on a "Cambridge Instruments" Stereoscan S250 Mk 3 microscope linked with energy dispersive X-ray analysis (EDAX) using a "Link systems" AN10000 energy dispersive X-ray system. The quantitative mineralogical composition of the contaminated surface and subsurface soil is presented in Table 3.5.

Table 3.4 Particle size analysis and selected other properties of the two soils used for further detailed studies

Soil depth (cm)	Clay (%)	Silt (%)	Sand (%)	CO_3 as $CaCO_3$ (%)	Total P (mg/kg)	Water holding capacity (%)
0-15	7.4	14.5	26.5	28.0	2400	80.4
50-90	37.7	18.4	42.6	nd*	310	97.7

*nd - not detected

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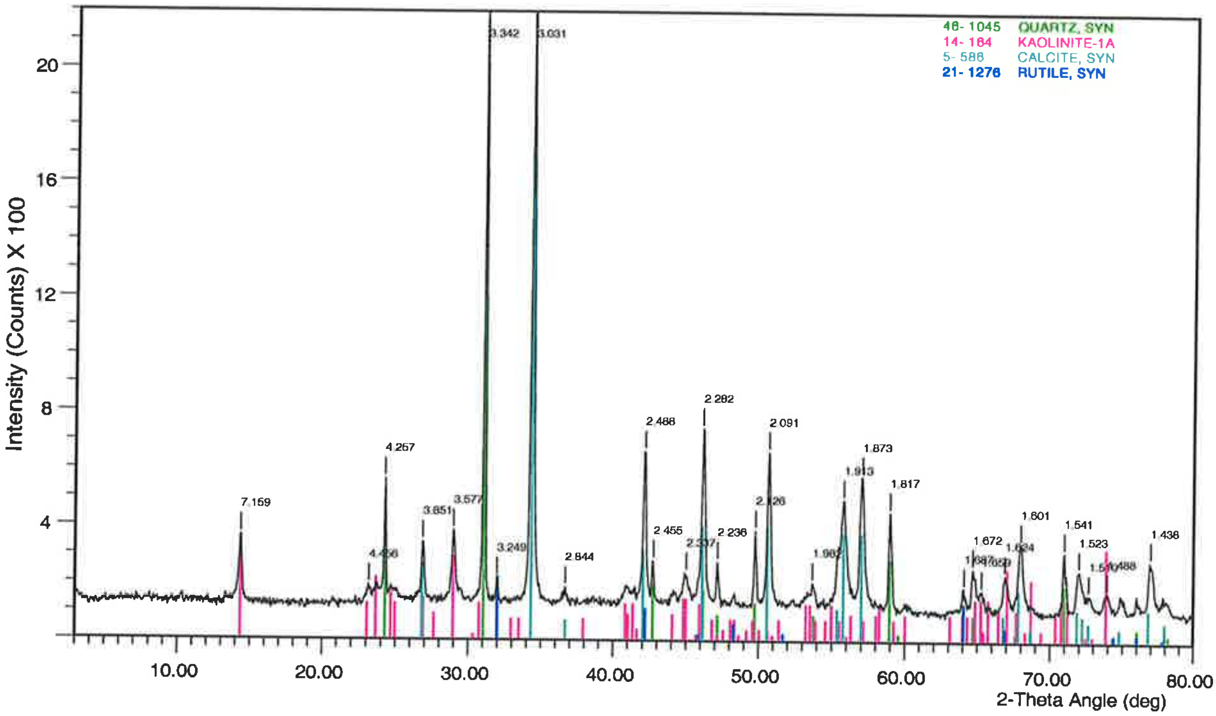


Fig. 3.6 X-ray diffraction pattern of the surface soil (0 – 15 cm)

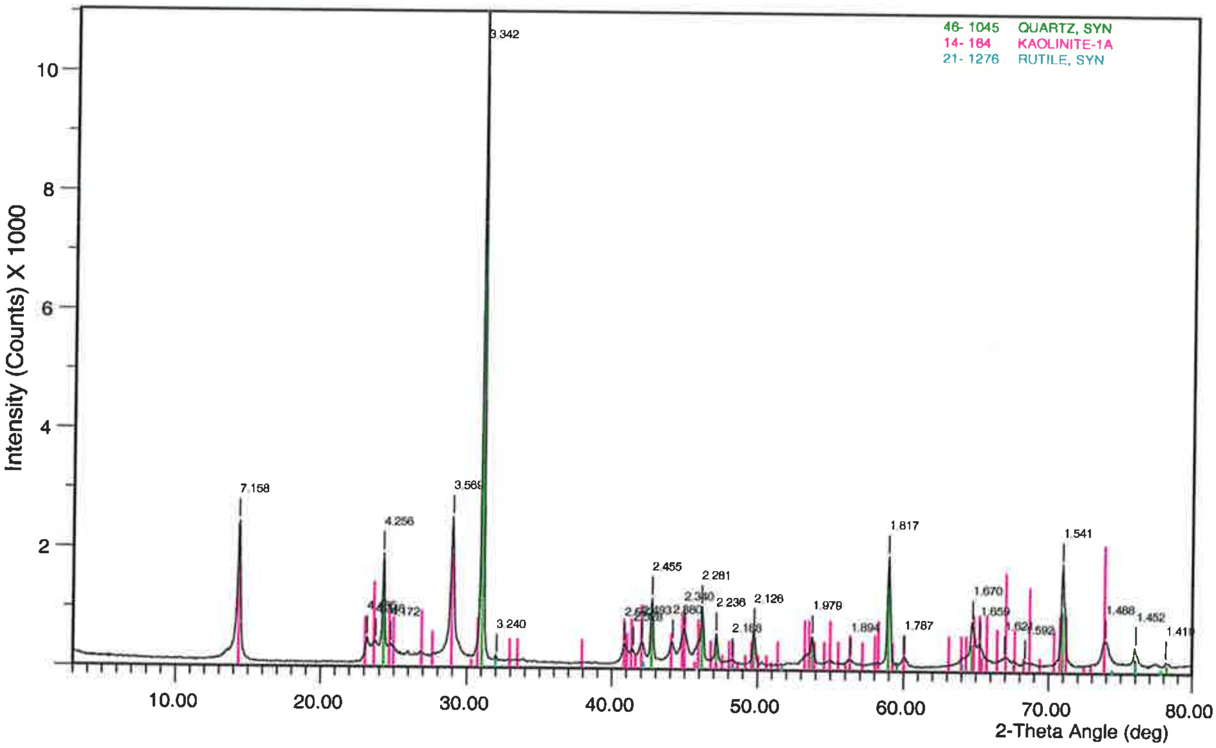


Fig. 3.7 X-ray diffraction pattern of the subsurface soil (50 – 90 cm)

Table 3.5 Quantitative mineral composition of the surface and subsurface soil used for the study

Mineral composition (%)	Surface horizon (0-15 cm)	Subsurface horizon (50-90 cm)
Amorphous material	66	<5
Calcite	15	nd*
Kaolinite	11	62
Quartz	8	38
Rutile	<1	<1

*nd – Not detected

3.2.4 Instruments and Analytical Conditions

Chromium analyses were performed with a GBC 906 (GBC Scientific, Melbourne, Australia) flame atomic absorption spectrometer (FAAS) and Varian Spectra 400Plus (Varian Australia Pty Ltd, Melbourne, Australia) and graphite furnace atomic absorption spectrometer (GFAAS) fitted with a Cr hollow cathode lamp as the radiation source. Generally, the recommended instrument parameters of the manufacturer were followed.

Soil solutions containing total Cr > 0.1 mg/L were continually analyzed using FAAS and where the total Cr concentrations < 0.1 mg/L samples were analyzed using GFAAS. The instrument parameters followed for FAAS and GFAAS are listed in Table 3.6. The total Cr(VI) in soil solutions was estimated using ion chromatography following the instrument conditions listed in Table 3.7.

Table 3.6 Instrument and flow rate settings for atomic absorptiton spectrometer

Instrument parameters	FAAS	GFAAS
Lamp Current (mA)	7	7
Fuel	Acetylene	Argon
Wave length	357.9	357.9
Slit Width (nm)	0.2	0.2
Slit Height	normal	normal
Flame stoichiometry	Reducing	nil
Absorbance	on	on
Background	off	off
Flow Rate (L/min)		
Acetylene	2.74	nil
Air	12.8	nil

Table 3.7 Instrument parameters for the analysis of chromate in Ion Chromatography

Column	Guard Column – Dionex Ionpac NGI Separator Column – Dionex IonPac
AS7	
Eluant	250 mM $(NH_4)_2SO_4$ 100 mM NH_4 Flow rate – 1.5 mL/min
Post-Column Reagent	2 mM Diphenylcarbohydrazide 10% v/v CH_3OH 1N H_2SO_4 Flow rate – 0.5mL/min
Detector	Visible 530 nm

3.2.5 Common Reagents and Methods

The standard stock solution of 1000 mg/L of Cr(VI) was prepared by dissolving 2.83 g of potassium dichromate salt ($K_2Cr_2O_7$) and diluting to 1L with deionised water. All other working standards were prepared from this stock solution by serial dilution with either deionised water or a solution of the background electrolyte being studied. Fresh standards and solutions were prepared for each experiment from the standard stock solutions and internal standards of the stock solution were prepared for analysis to confirm that degradation of the standard stock solutions had not occurred. The standard stock solution of 1000 mg/L of Cr(VI) was periodically replaced as described above. The same standard stock solutions were used as standards for the estimations of total Cr and Cr(VI) in soil solutions. The concentrations of all working standards were periodically verified against Spectrasol™ standards.

Precautions were taken during the analyses of soil solutions to minimise contamination. All plastic and glassware were washed with deionised water, soaked for 16 h in 2 M HCl solution, rinsed again with deionised water and oven dried at 60 ^{0}C before use.

Chromium was not detected in the blank solutions analysed prior to and during the analyses of all sample solutions, confirming no Cr contamination. Standard reference materials and blanks were included in all runs at a rate of at least 5% in all experimental runs.

CHAPTER 4

Nature of Chromium Interactions in the Long-term Tannery Waste Contaminated Soil

4.1 Introduction

The tannery waste contaminated site at Mount Barker consists of a complex mixture of organic and inorganic constituents with Cr as the major contaminant. Remediation strategies currently adopted in managing metal contaminated soils include *ex-situ* soil washing, *in-situ* chemical immobilization and bioremediation of the contaminants at the site. However, all of these techniques are prohibitively expensive. For this reason, there is now a move towards monitored natural attenuation of contaminants. Such a strategy requires a thorough understanding of the binding between contaminants and soil constituents that control contaminant bioavailability. If the contaminants are tightly bound, the bioavailability is generally low and if it does not change with environmental fluctuations viz. moisture, pH etc., sites are declared safe.

In this study, we aim to investigate the structural components of the soil to which Cr is bound. Information on Cr-soil interactions will help evaluate the strength of these bonds, which is a useful first step in developing strategies for managing contaminated sites. Also, in order to estimate the bioavailability of Cr and its potential toxicity it is desirable not only to determine the total concentration but also the different chemical forms and binding mechanisms between Cr and the solid phase. It is these interactions that control the release and uptake of Cr in the contaminated soil.

Sequential extraction has been commonly used to assess the relative distribution of metals or non-metals amongst the different soil components (Pickering, 1986 and Bermond and Yousfi, 1997). Despite some limitations associated with sequential extraction techniques (re-adsorption among the phases during the extraction, poor reagent selectivity, operating conditions affecting the extraction and difficulty of comparing results from different methods), they have been widely accepted for metal fractionation in soils and sediments (Fernandez Albores et al., 2000). In multiple extraction techniques, different chemical extractants are sequentially applied to a test sample, each follow-up treatment being either more drastic in chemical action or different in nature from the previous treatment (Zufiaurre et al., 1998). Many of these extraction schemes are based on the five-stage Tessier et al. method or its modifications (Tessier et al., 1979). These sequences are designed to differentiate between the exchangeable, carbonate, reducible (hydrous Fe/Mn oxides), oxidizable (sulfides and organic phases) and residual (mineral) fractions. The main modification suggested by subsequent researchers was to differentiate the Fe and Mn oxide bound species into three distinct phases, namely, easily reducible metal oxide bound, amorphous metal oxide bound and crystalline metal oxide bound species (Sposito et al., 1982; Shuman, 1985; Gibson and Farmer. 1986; Kersten and Forstner, 1986 and Elliott et al., 1990). Many studies have used sequential extraction techniques to remove metals in cationic form from soil components (Miller and McFee, 1983; Hickey and Kittrick, 1984; Miller et al., 1986 and Krishnamurthi et al., 1995). However, few studies have developed a sequential extraction scheme for Cr that forms both cationic and anionic species in soils (Asikainen and Nikolaidis, 1994; Wasay et al., 1998; Hughes and Noble, 1991; Xiao-Hou et al., 1993; Philips and Chapple, 1995). Apart from these, only a limited number of studies have been conducted using sequential extraction schemes in contaminated soil situations (Reddy and Chinthamreddy, 2000; Dudka and Chlopecka, 1990; Thangavel and Naidu, 2000). In order to propose and implement effective remedial measures for a contaminated site it is necessary to investigate the partitioning of the contaminant in the soil. The objective of this investigation was to quantitate the relative partitioning of Cr amongst the different soil components in the tannery waste contaminated soil of Mount Barker using a sequential extraction scheme.

4.2 Materials and Methods

Surface (0-15 cm) and subsurface (50-90 cm) oven dried (40°C) soils (< 2 mm) were used to investigate the nature of interactions between Cr and soil constituents. These soils provided contrasting pH, organic matter content and mineral composition. Detailed physico-chemical properties of the soils were presented in Chapter 3; selected properties relevant to this chapter are listed in Table 3.3.

4.2.1 Fractionation

The sequential extraction was carried out, in triplicate, on 1.5 g of the contaminated surface and subsurface soil in 40 mL polyethylene centrifuge tubes in order to facilitate centrifuge-washing of the soil after each extraction thus minimizing any loss of the solids. Prior to and after each extraction process, the tubes plus soil and cap was weighed to account for entrained solution. After each successive extraction, the supernatant was removed by centrifugation for 10 min at 15000 rpm (32570 G). The residue was washed with 10 mL of deionised water, centrifuged for 10 min at 15000 rpm (32570 G) and the supernatants combined, mixed and made up to a known volume. The analysis of the data was carried out on the average values of the triplicate samples.

Deionised water was used in preparing stock solutions of all the reagents. All the reagents used were of analytical grade and were checked for possible trace metal contamination by analysing a blank during every analysis.

4.2.2 Chromium Speciation in the Extract

The nature of Cr present in the water extracts and exchangeable Cr fraction were estimated using ion chromatography. Initially the solutions were analysed for total Cr using both FAAS or GFAAS. Solutions from the remaining steps were analysed for total Cr using FAAS or GFAAS alone. The methods used for the analyses of total Cr and Cr(VI) are described in detail in Chapter 3.

4.2.3 Total Cr in the Soil

For total Cr analysis the soils were ground in an agate mortar and homogenised before use. Because the contaminated soil had a high organic carbon content smaller quantities of soils were used for the total Cr analysis. Surface soil (0.1 g) and sub surface soil (0.2 g) were digested in a teflon beaker by adding HF (10 mL) and $HClO_4$ (1 mL) until the suspension was nearly dry (Tessier et al., 1979). The residue was dissolved in 6 N HCl (5 mL) and made up to a known volume with deionised water. The resulting solution was analysed by FAAS using the method described in Chapter 3. Samples were analysed in duplicate.

4.3 Sequential Extraction Scheme

The sequential fractionation scheme of Krishnamurti et al., (1995) was used to speciate particulate-bound Cr in soils. This scheme was based on that proposed by

Tessier et al., (1979) and Shuman (1985) but was a modified to suit both species of Cr found in the contaminated soil. The fractionation procedure is outlined in Table 4.1.

Table 4.1 Sequential Extraction Scheme used for Cr fractions from tannery waste contaminated soil

Step	Fraction	Reagents	Shaking time and temperature
1	Water Soluble	30 mL of Deionised water	6 h at 25 ± 2 °C
2	Exchangeable – Step 1	30 mL of 0.01 M KH_2PO_4/K_2HPO_4	16 h at 25 ± 2 °C
3	Exchangeable – Step 2	20 mL of 1 M $Ca(NO_3)_2$	4 h at 25 ± 2 °C
4	Carbonate bound	25 mL of 1 M CH_3CO_2Na (pH 5)	6 h at 25 ± 2 °C
5	Metal-organic complex	30 mL of 0.1 M $Na_2P_2O_7 \cdot 10\,H_2O$ (pH 10)	20 h at 25 ± 2 °C
6	H_2O_2 extractable organic-bound	5 mL of 30% H_2O_2 (pH 2), 3 mL of 0.02 M HNO_3; then add 3 mL of 30% H_2O_2; cool, add 10 mL of 1 M NH_4NO_3 in 20% HNO_3	2 h at 85 °C 2 h at 85 °C 0.5 h at 25 ± 2 °C
7	Fe and Mn oxides bound	25 mL of 0.2 M $(NH_4)_2C_2O_4$ + 0.2 M $H_2C_2O_4$ (pH 3) in 0.1 M $C_6H_8O_6$	0.5 h at 95 °C
8	Residual	Residue of step 6 digested with HF-$HClO_4$	

4.3.1 Sequential Extraction Scheme used in the Present Study

4.3.1.1 Step 1. Water Soluble

Firstly, deionised water was used to extract the water-soluble Cr present in the soil, and then speciation of Cr was investigated following the methods described in Chapter 3.

4.3.1.2 Step 2. Exchangeable Fraction – Step 1

In most of the earlier sequential extraction schemes 1 M $MgCl_2$ (pH 7), 1 M $Mg(NO_3)_2$ (pH 7) and 0.5 M $MgCl_2$ (pH 7) were used to extract the exchangeable Cr fractions from soils and sludge samples (Fernandez Albores, 2000; Maiz et al., 1997; Xiao-Hou, 1993; Zufiaurre et al., 1998). Asikainen and Nikolaidis (1994) used a 0.01 M potassium-phosphate buffer to extract exchangeable Cr from aquifer sediments. For the exchangeable Cr fraction James and Bartlett (1983c) have also recommended a potassium-phosphate buffer as an extractant. This extractant seems to be ideal. It is buffered at pH 7.2 and therefore tends to minimize iron and manganese oxide and organic matter dissolution. Additionally, the dominant phosphate species, HPO_4^{2-} and $H_2PO_4^-$, favor desorption of $HCrO_4^-$ and CrO_4^{2-} species by anion exchange (Eary and Rai, 1989). Therefore, in the present study, for the exchangeable fraction of Cr(VI), 0.01 M KH_2PO_4/K_2HPO_4 buffered at pH 7.2 was used as the extractant. The phosphate buffer extracts were assessed for both total and speciated Cr. This was considered important given that the exchangeable pool controls the release of Cr to soil pore water and it is this fraction that requires remediation for the management of contaminated sites. Following extraction the tube and the contents were weighed to account for entrained solution.

4.3.1.3 Step 3. Exchangeable Fraction – Step 2

Following extraction of the exchangeable fraction of Cr(VI) the residue was extracted with 1 M $Ca(NO_3)_2$. This extraction targets the exchangeable Cr(III) present in the surface soil. This assumes that the divalent cation, Ca^{2+}, would be a more effective extractant for exchangeable Cr(III) than K^+ in the potassium-phosphate buffer used in the previous step.

4.3.1.4 Step 4. Carbonate-bound

Selective dissolution of carbonates from soil and sediment samples was carried out using 1 M CH_3CO_2Na-CH_3CO_2H solution at pH 5.0 (Tessier et al., 1979; Gibson and Farmer, 1986; Elliott et al., 1990). Dudka and Chlopecka (1990) and Fernandez Albores et al., (2000) have demonstrated the utility of NaOAc to extract Cr bound to the carbonates in their sequential extraction studies with sludge-amended soils. The same procedure was adopted in this study.

4.3.1.5 Step 5. Metal-organic Complex-bound

In all existing sequential extraction schemes the next step was to extract metal bound to the Fe and Mn oxides (Tessier et al., 1979; Gibson and Farmer, 1986; Elliott et al., 1990). However, certain metal oxides are bound to organic components and exist as metal-organic complexes, which can be extracted by pyrophosphate (Bascomb, 1968; McKeague, 1967). Limited attention has been paid to the Cr species bound to the metal-organic complexes in the fractionation schemes used so far. Asikainen and Nikolaidis, (1994) used pyrophosphate for organic bound Cr in aquifer sediment samples. To remove the precipitated Cr, they used a 0.05 M HCl wash after the pyrophosphate step. However, in the present study, the Cr bound to the metal-organic complexes was extracted using sodium pyrophosphate. A solution of sodium or potassium pyrophosphate was earlier proposed as a specific reagent for the removal of Fe and Al organic complexes (Bascomb, 1968; McKeague, 1967). In this study a solution of 0.1 M sodium pyrophosphate at pH 10.0 was used to extract Cr bound to metal-organic complexes.

4.3.1.6 Step 6. Organic-bound

The destruction of organic matter is commonly achieved by using 30% H_2O_2 in a mildly acidic medium with boiling on a water-bath (Jackson, 1958). As released metal ions could be re-adsorb onto soil mineral components, subsequent extraction with an indifferent electrolyte solution, such as $CH_3CO_2NH_4$ was recommended (Tessier et al., 1979; Kersten and Forstner, 1986). In the present scheme, 30% H_2O_2 was used for the extraction of the Cr bound to residual organic matter, followed by washing with a solution of 1 M NH_4NO_3 to release the Cr ions sorbed on to the soil mineral components.

4.3.1.7 Step 7. Crystalline Fe oxide-bound

Sodium citrate-dithionate-carbonate (pH 7.3) was suggested as a suitable reagent for removing Fe oxides (Mehra and Jackson, 1960). However, the dithionate salt is usually contaminated with metal impurities and metal ions can be lost from solution through metal sulphides (Shuman, 1982; Tessier et al., 1979). Shuman (1982) showed that a solution of 0.2 M ammonium oxalate adjusted to pH 3 with oxalic acid in the presence of 0.1 M of ascorbic acid extracted amounts of Fe similar to that of the dithionate reagent. Hence, in the present study the same extractant used by Shuman (1982) was used to extract the Cr bound to crystalline Fe oxide.

4.3.1.8 Step 8. Residual

The residual Cr resistant to the above successive sequential extraction was determined using HF-$HClO_4$ digestion (Tessier et al., 1979). The detailed procedure is discussed in Section 4.2.3 of this chapter.

4.3.2 Nature of Cr-organic Matter Interaction

Solid phase fractionation studies revealed unusually high partitioning of Cr with the organic matter fraction. In order to understand better the mode of interaction and binding between organic matter and Cr a detailed solid state ^{13}C NMR spectroscopic study of tannery waste was conducted. Solid state ^{13}C NMR spectra were acquired for three samples; tannery sludge, bulk topsoil and HF treated topsoil. HF treatment removes most of the mineral component of the soil and improves the quality of NMR spectra by (i) concentrating the organic fraction and (ii) removing paramagnetic species, which adversely affect NMR observability.

The objective of using NMR spectroscopy was to (i) investigate the chemical nature of the organic matter in the tannery sludge and sludge-affected topsoil and (ii) probe the interactions between the organic matter and the Cr used in the tanning process.

4.3.2.1 Materials and Methods

4.3.2.1.1 Sample Preparations

The green coloured, lightweight material found in the surface soil was separated physically and treated as the tannery sludge sample. The < 2 mm oven dried (40°C) surface soil (0 – 15 cm) was treated as bulk top soil and the same soil was treated with 2% HF to remove the paramagnetic Fe and Cr and to concentrate the organic matter (Skjemstad et al., 1994). All the samples were finely powdered in an agate mortar.

4.3.2.1.2 Instrumentation and Analytical Techniques

Solid state ^{13}C CPMAS (cross polarisation, magic angle spinning) and Bloch decay NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000 ± 100 Hz in a Doty Scientific MAS probe. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. For the CP spectra, a 1 ms contact time and an 500 ms recycle delay were used for each sample. Between 20000 and 100000 transients were collected for each sample. A 90 s recycle delay was used for the Bloch decay spectrum, and 1000 transients were collected. The Bloch decay spectrum was corrected for background signal by subtracting the Bloch decay spectrum of an empty rotor. All spectra were zero filled to 8192 data points and processed with 50 Hz Lorentzian line broadening and a 0.010 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

4.3.2.1.3 Spin Counting and T_1H Relaxation Rates

$T_{1\rho}H$ relaxation rates were determined from variable contact time experiments, according to the method of Smernik and Oades (2000a). Spin counting was performed according to the method of Smernik and Oades (2000a), using glycine as an external reference. Average (1 component) T_1H relaxation rates were determined from inversion-recovery experiments according to the method of Smernik and Oades (2000c). To specifically obtain T_1H relaxation rates for Cr(III), a 0.5 M solution of $CrCl_3$ was reacted with 0.5 g collagen and examined following the procedure described by Smernik and Oades (2000c). The freeze dried material thus obtained was used to estimate the T_1H relaxation rates for collagen and Cr(III). Between 10000 and 20000 transients were collected per recovery delay; a total of 10 recovery delays between 0.1 ms and 1 s were used.

4.4 Results and Discussion

4.4.1 Total Cr Content of the Soils

The mean total Cr concentration estimated by the $HF-HClO_4$ dissolution of the surface and subsurface soil was 91035 mg/kg and 471 mg/kg respectively.

The total Cr extracted by $HF-HClO_4$ was higher than that extracted by aqua-regia from both the surface and subsurface soil of the contaminated site. The enhanced removal of Cr by $HF-HClO_4$ was achieved because of the complete dissolution of detrital silicate minerals, resistant sulphides and a small quantity of refractory organic material (Tessier et al., 1979). These results clearly demonstrate that aqua-regia digests do not reflect total metal contents.

4.4.2 Partitioning of Cr

The particulate-bound Cr speciation in the contaminated surface and subsurface soil, as determined by the sequential extraction scheme mentioned above is presented in Table 4.2.

Table 4.2 Sequential extraction of Cr from contaminated surface and subsurface soil

Fraction	Chromium (mg/kg of soil)[a]	
	Surface Soil	Subsurface Soil
Water soluble	4 (0.1)	0.38 (0.1)
Exchangeable Cr – Step 1*	10 (0.2)	0.21 (0.03)
Exchangeable Cr – Step 2**	10.76 (0.15)	9.76 (0.07)
Carbonate-bound	230 (5.5)	2.98 (0.09)
Metal-organic complex-bound	417 (2.8)	8.24 (0.24)
H_2O_2 extractable organic-bound	90832 (2860)	194.93 (8.91)
Crystalline Fe and Mn oxide bound	6857 (660.2)	32.55 (4.75)
Residual	833 (117.4)	181.5 (1.5)

* Mainly target the exchangeable Cr(VI); ** Mainly targets the exchangeable Cr(III)
a - Mean and standard deviation (in parenthesis) of three replicates.

The total Cr present in the subsurface soil was only 0.5% (471 mg/kg) of the total Cr present in the surface soil (91035 mg/kg). With one exception, the mean relative abundance of particulate Cr in the various soil components followed the same general trend; it is the residual fraction in surface soil that is greater than the metal-organic complex bound Cr that shows reverse trend in the subsurface soils. The proportion of Cr associated with the different soil components however, varied appreciably between the surface and subsurface soils as shown below:

Surface Soil

H_2O_2 extractable organic-bound (91.6%) > Crystalline Fe and Mn oxide-bound (6.9%) > Residual (0.84%) > Metal-organic complex bound (0.42%) > Carbonate-bound (0.23%) > Exchangeable Cr- step 2 (0.01%) > Exchangeable Cr- step 1 (0.01%) > Water-soluble (0.004%).

Subsurface Soil

H_2O_2 extractable organic-bound (45.3%) > Residual (42.2%) > Crystalline Fe and Mn oxide-bound (7.56%) > Exchangeable Cr- step 2 (2.3%) > Metal-organic complex bound (1.9%) > Carbonate-bound (0.69%) > Water-soluble (0.09%) > Exchangeable Cr- step 1 (0.05%).

As shown above, Cr in the surface soil was predominantly partitioned into the H_2O_2 extractable organic-bound fraction. This accounted for 91.6% of the total Cr present in the soil. Similarly, the Cr in the contaminated subsurface soil was predominantly partitioned into the H_2O_2 extractable organic-bound fraction. However, equal proportions of Cr were partitioned in the residual fraction of the subsurface soil. Unlike the surface soil where 91.6% of the Cr was partitioned in H_2O_2 extractable organic-bound fractions, nearly 80% of the total Cr was partitioned in the H_2O_2 extractable organic-bound fraction and residual fraction of the subsurface soil. All other fractions namely, carbonate bound (0.7%), metal-organic complex bound (1.9%) and crystalline Fe and Mn oxide bound (7.6%) fractions were of small proportion compared to the sum of Cr fractions in the subsurface soil.

4.4.3 Speciation of Cr

In both surface and subsurface soils the proportion of water extractable and exchangeable Cr was low compared to total Cr present in the soil. However, speciation of Cr, into hexavalent and trivalent forms was carried out only for these fractions within the entire sequential extraction scheme. This is because, from the exchangeable fraction - step 2 onwards, extractants used could possibly induce transformation of Cr species in the soil.

Speciation of Cr in the water extractable and exchangeable fractions showed contrasting results between surface and subsurface soils. While Cr in the alkaline surface soil was predominantly in the hexavalent form, the species present in the strongly acidic subsurface soil was predominantly in the cationic Cr(III). It is therefore likely that any Cr(VI) leached from the surface soil is transformed into Cr(III) due to the acidic soil pH (3.9), the prevalence of reductants including Fe and S (Saleh et al., 1989) and the low redox conditions in the subsurface layers. Only 0.1% of the total Cr in the subsurface soil was extractable in water and the concentration of Cr in exchangeable Cr was extremely low (0.05%). Generally Cr(III) is held tightly through covalent bonds and its displacement is difficult in water extracts (Draljaca et al., 1992). Also Cr(III) has a tendency to hydrolyse and spontaneously form polynuclear complexes containing OH bridges (Cotton and Wilkinson, 1980). The low extraction of exchangeable Cr by potassium-phosphate buffer shows that potassium may not be an effective cation for exchanging Cr(III) from exchangeable sites. However, when 1 M $Ca(NO_3)_2$ was used to extract exchangeable Cr- step 2, nearly 9.8 mg/kg of Cr(III) was extracted which is nearly 2% of the total Cr present in the subsurface soil.

Similar trends in the distribution of Cr(VI) and Cr(III) in the surface and subsurface contaminated soils from the same site were recently reported by Kookana et al., (2000) in their intact core studies. Although the proportion of water extractable Cr is small with respect to total Cr present in the contaminated soil, the concentration of water extractable Cr(VI) was five times higher than the maximum threshold limit set for drinking water standards. Moreover the high mobility of Cr(VI) in alkaline surface soil would favour migration of this toxic form of Cr to subsurface layers and eventually may contaminate the groundwater aquifers in the area.

4.4.4 Exchangeable Cr – Step 1

Exchangeable Cr in the first instance was estimated using the potassium-phosphate buffer solution. James and Bartlett (1983c) has demonstrated that the phosphate present in the potassium-phosphate buffer effectively competes with CrO_4^{2-} or $HCrO_4^-$ for the exchange sites. The amount of phosphate extractable exchangeable chromate was small compare to the total Cr present in the contaminated soil (Table 4.2). Nevertheless, the amount of exchangeable Cr present in the surface contaminated soil was high. Given that exchangeable Cr represents the pool of Cr that is potentially mobile, the large pool of exchangeable Cr poses a risk to both surface and groundwater quality. This risk is further exacerbated by the speciation data, which shows that all the phosphate extractable Cr was present as Cr(VI).

Asikainen and Nikolaidis (1994) used a potassium-phosphate buffer to extract exchangeable Cr from aquifer sediments and they expected that the potassium present in the buffer would effectively remove the exchangeable Cr(III) as well from the exchangeable sites. However, they did not report any speciation of Cr in their studies to prove that potassium-phosphate buffer could be effective in extracting both stable species of Cr from soils.

4.4.5 Exchangeable Cr – Step 2

In the present sequential scheme 1 M $Ca(NO_3)_2$ was used after the phosphate extraction to target the exchangeable Cr(III). Appreciable release of Cr from the contaminated surface soil was observed. Because this extractant had such a high ionic strength, aqueous speciation of Cr was not carried out for this fraction. The amount of extractable Cr released in this fraction was 10.8 mg/kg in the surface soil. Compared to total Cr, the amount released in the extract is rather small although there is potential for release of this fraction into soil pore water. Given that the different pools of Cr are linked to each other by partition coefficients and Le Chatellier's principle, the fraction of Cr present in soil pore water is likely to be controlled by each of the soil constituents binding Cr in soils.

Cr bound to the H_2O_2 extractable organic fraction was the dominant fraction, accounting for 91% of the sum of individual fractions of Cr from surface soil. Most of the studies on sequential extraction schemes for Cr fractions in soils mixed with sludge have reported that Cr was predominantly found to be associated with the H_2O_2 extractable organic fraction (Zufiaurre et al., 1998; Dudka and Chlopecka, 1990; Fernandez Albores et al., 2000; Maiz et al., 1997). In this contaminated site the presence of 10% organic carbon and the source of Cr through dumping of tannery wastewater would support the association of Cr predominantly found with H_2O_2 extractable organic fraction in the surface soil. The amount of Cr associated with the organic matter fraction could potentially release the metal into soil solution under strong oxidising conditions (Ure and Davidson, 1995).

The carbonate bound fraction (0.23%), metal-organic complex bound (0.42%) and crystalline Fe and Mn oxide bound fractions (7%) are small compared to the sum of all fractions. However, we have to consider that these fractions could also become available under suitable soil conditions. The Cr bound to the residual fraction was 0.8% compared to the total and this fraction corresponds to the part of the Cr that cannot be mobilised.

4.5 Organic Matter-Cr Interactions

The unusual partitioning of higher amounts of Cr in the H_2O_2 extractable organic fraction and also the potential release of Cr under oxidising conditions prompted us to characterise the quality of organic matter present in the contaminated surface soil. A solid state ^{13}C CP/ MAS NMR study was carried out to investigate qualitatively the nature of organic matter present and explore the Cr binding strength in this fraction.

4.5.1 The Nature of the Organic Matter

^{13}C CPMAS (cross polarisation with magic angle spinning) NMR spectra of the three samples (Fig. 4.1) are quite similar to each other, and significantly different to samples of "normal" soil organic matter. In each spectrum, the strongest resonance is in

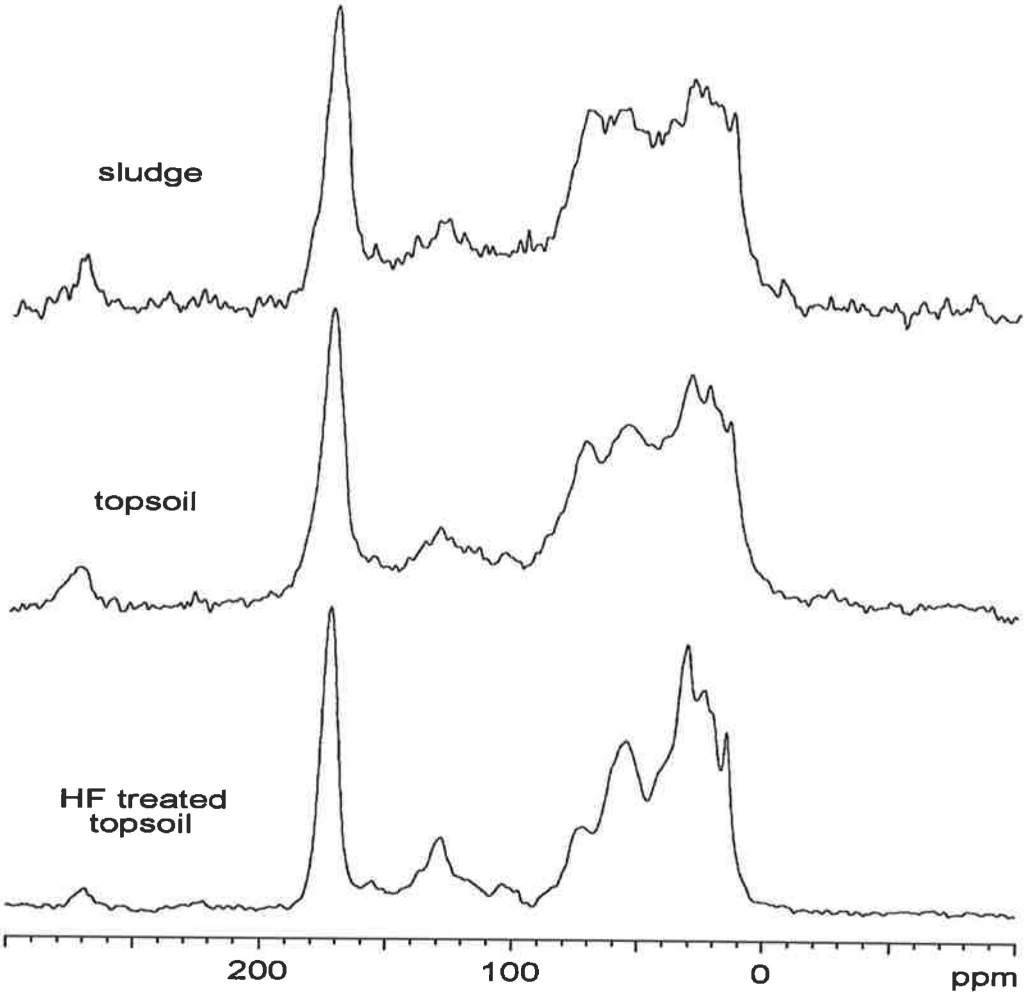


Fig. 4.1 ^{13}C CPMAS NMR spectra of sludge, topsoil and HF treated topsoil

the carbonyl region at ~173 ppm. A weak resonance at 128-130 ppm is due to aromatic or alkene carbons. The resonance at ~73 ppm is probably due to the carbohydrate carbon, as it is significantly weaker in the HF treated soil sample than in the other two samples. A broad resonance centered at 54-57 ppm is most likely due to the carbon adjacent to the amide nitrogen in the amino acid residues of protein structures. Three prominent peaks are observed in the alkyl carbon region, at 30, 23 and 15 ppm most likely due to methylene (30 ppm.) and methyl (23, 15 ppm) carbons. The spectra are very similar to that of collagen (Smernik and Oades, 2000a), indicating a predominance of protein structures.

4.5.2 Effects of Chromium on NMR Spectra

Paramagnetic species effect NMR spectra through the interaction of the spin of the unpaired electron of the paramagnetic species with the nuclear spin of ^{13}C and ^{1}H nuclei. The results of this interaction include NMR signal loss, signal broadening and increased relaxation rates. Since Cr(III) is a paramagnetic species, the presence of bound Cr(III) will affect the ^{13}C NMR spectra of the organic matter.

To assess the effect of Cr(III) on the observability of the NMR spectra, spin counting experiments were carried out. This involves comparing signal (per unit carbon) against that of a reference sample (glycine). The relative observability of ^{13}C CPMAS NMR signal from the three samples was low compared to that of model compounds and soil organic matter samples (Smernik and Oades, 2000a,b). HF treatment of the topsoil sample did improve observability from 20% to 44% (Table 4.3), however this latter value is still very low. NMR observability increased with decreasing concentrations of Cr, being lowest for the sample highest in Cr (sludge, 7.9% Cr, CP

Table 4.3 **Results of spin counting experiments**

Sample	Mass (mg)	%C	C (mg)	CP signal[a]	CP observability	BD signal	BD observability
Glycine	367	32.0	117.5	121.4	100%	39.9	100%
Topsoil	343	12.4	42.5	9.0	20%	n.d.	-
HF treated	237	29.8	70.7	32.4	44%	16.9	70%
Sludge	306	15.8	48.4	8.6	17%	n.d.	-

[a] Corrected for differences in $T_{1\rho}H$ relaxation rates according to Smernik and Oades, (2000a)
n.d. not determined

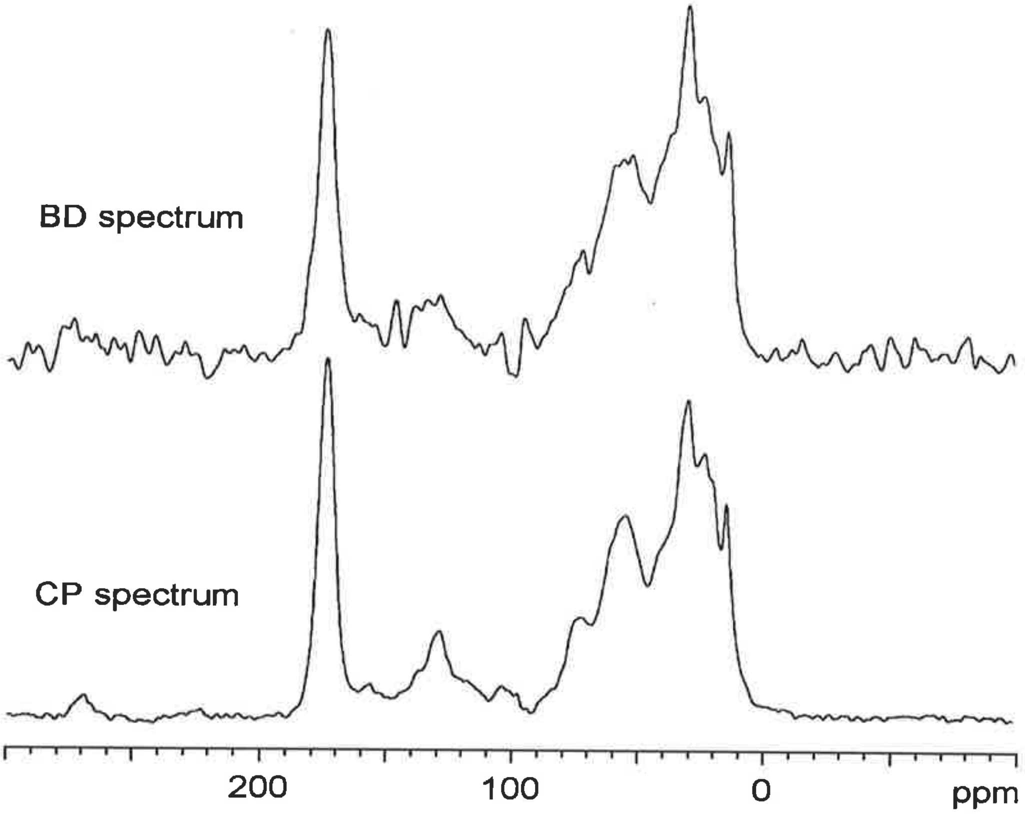


Fig. 4.2 Comparison of Bloch decay and CPMAS spectrum for HF treated sample

observability 17%), followed by topsoil (4.8% Cr, CP observability 20%), then HF treated topsoil (0.5% Cr, 44% CP observability).

A Bloch decay spectrum was acquired for the HF treated soil sample. This spectrum is similar to the corresponding CPMAS spectrum, except for a slightly more intense resonance at 30 ppm (Fig. 4.2). This may indicate the presence of lipids with a high degree of molecular mobility, which can be underestimated by the CPMAS technique (Smernik and Oades 2000a). Spin counting on the Bloch decay spectrum indicated that 70% of potential NMR signal was observed (Table 4.3).

T_1H relaxation rates are very sensitive to the presence of paramagnetic species (Smernik and Oades 2000c). Average T_1H relaxation rates for the three samples were very similar, falling in the range 8.9-11.3 ms (Table 4.4). These values are 2 orders of magnitude shorter than that observed for collagen (T_1H = 1011 ms), but are similar to that of collagen amended with 2% Cu^{2+} (T_1H = 14.1 ms) (Smernik and Oades 2000c). The T_1H relaxation rates obtained for collagen amended with Cr^{3+}(T_1H = 7.4 ms) was close to the T_1H relaxation rates of HF treated samples. This clearly indicated that the organic matter may contain a large concentration of tightly bound Cr^{3+}, even after HF treatment.

Table 4.4 Average T_1H relaxation rates

Sample	Average T_1H (ms)
Topsoil	10.5
HF treated	8.9
Sludge	11.3
Collagen	1011.0[a]
Collagen + Cu^{2+}	14.1[a]
Collagen + Cr^{3+}	7.4[a]

[a] Smernik and Oades 2000c

4.6 Conclusions

The following key findings were elucidated from the results:

a) Total Cr concentration exceeds 9% in the contaminated surface soil and 0.05% in the subsurface horizon;

b) There is extensive contamination of the surface and subsurface soils at the Mount Barker tannery waste disposal sites;

c) There is high Cr bioavailability at the contaminated sites;

d) There are large concentrations of exchangeable Cr(VI) indicating potentially large sources of Cr bioavailable over a long period;

e) More than 91% of the Cr is associated with organic matter;

f) Solid state NMR studies confirm that Cr is strongly bound to the predominantly proteinecious organic matter of the contaminated soil.

CHAPTER 5

Effects of Electrolyte Composition on Chromium Desorption in Soils Contaminated by Tannery Waste

5.1 Introduction

There are conflicting reports in the literature regarding the impact of disposal of tannery waste to land or water resources. In some studies no significant adverse effect was reported on crops grown on agricultural soils applied with chromium tannery waste or under long term application of sewage sludge containing Cr (Chaney et al., 1981; James and Bartlett 1984; Hemphill et al., 1985; Berti and Jacobs 1996, 1998). Conversely, some studies have shown that tannery waste disposal has led to severe contamination of productive agricultural land in Bangladesh, India (Mahimairajah et al., 2000) and in Australia (Naidu et al., 2000a). These studies have implications to Cr bioavailability and potentially impact on environmental health since Cr can potentially leach offsite and contaminate surrounding surface and ground water.

Chromium is frequently one of the more toxic elements present in tannery waste. It is generally understood that Cr(III) is less toxic than Cr(VI). Hexavalent chromium, Cr(VI), is mainly produced by industrial processes and has been classified as a human carcinogen if inhaled. Specifically, exposure to certain water-insoluble and water-soluble Cr(VI) compounds is associated with lung cancer in humans (IARC, 1990; Cohen et al., 1993; Langard, 1993). It is generally believed that there is little potential for Cr(VI) contamination of groundwater resulting from the disposal of tannery or sewage sludge to soils (Money, 1991), because generally Cr in such wastes is generally expected to exist primarily as Cr(III), which is the relatively immobile species.

It is clearly evident from Chapter 4 that appreciable amounts of water soluble and exchangeable Cr(VI) is released from the surface soil at the contaminated site. Of major concern is the alkaline nature of subsurface soils. Under alkaline pH and also considering the slow persistent rainfall during the winter months in Adelaide, there is some concern that leaching of water-soluble Cr(VI) may pose a risk to groundwater. Indeed earlier studies by Naidu et al., (2000b) reported the presence of appreciable levels of Cr in subsurface water samples. Equally high Cr concentrations were reported in soils surrounding tannery waste disposal sites in India, where Cr(VI) was detected in the groundwater (Mahimairajah et al., 2000). The presence of Cr (VI) in surface and subsurface water bodies at these tannery waste disposal sites is surprising, given that Cr(III) salts were used during the tanning process. Such salts are considered immobile and thermodynamically stable relative to Cr(VI) (Naidu and Kookana, 2000). According to Bartlett and James (1979), in soils Cr(III) may oxidize to Cr(VI) only in the presence of Mn(IV). Among the factors that have been reported to influence Cr desorption and mobilization are pH and the presence of strong ligand ions such as phosphate (Weng et al., 1994, Bartlett and James, 1988; Stollenwerk and Grove, 1985). The presence of Cr(VI) in both the soil and water bodies at the contaminated site at Mount Barker prompted us to investigate factors that influenced the release and mobilization of Cr in soils.

Since tannery wastes generally contain elevated concentrations of, Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, and PO_4^{3-} (UNEP and IEO, 1991), the following objectives were addressed in the present study:

1. To examine the effects of solution cations, Ca^{2+} and Na^{+}, of similar ionic strength, on the desorption behavior of Cr(VI) from contaminated surface soil and the desorption behaviour of Cr(III) from subsurface soil, and
2. To examine the desorption behaviour of Cr from the surface and subsurface soil in the presence of anions, chloride and varied concentrations of phosphate.

5.2 Materials and Methods

5.2.1 Soils

The surface (0 – 15 cm) and subsurface (50 – 90cm) soils were sieved < 2 mm and dried at 40°C in a fan-forced oven. Soils were collected from a 1.5 m deep soil pit excavated on site and were used for all desorption experiments. Pertinent properties of the soils and soluble salt concentration in 1:5 soil:water extracts extracted after 1h equilibration are given in Table 5.1. The detailed soil physico-chemical properties are presented in Table 3.3 and 3.4, in Chapter 3.

Table 5.1 Some relevant properties of the soils used for the desorption experiments

Depth (cm)	pH[a]	EC (dS/m)	Cr(VI)[a] (μg/mL)	Ca[a] (μg/mL)	Mg[a] (μg/mL)	Na[a] (μg/mL	P[a] (μg/mL)	S[a] (μg/mL)
0-15	7.9	0.67	0.43	125.4	2.96	7.08	0.01	63.4
50-90	3.9	0.98	nd*	142	9.4	49.4	0.01	149.4

*nd – not detected: a - 1:5 soil:water extract

5.2.2 Soil and Soil Solution Analysis

Soil and soil solution were analysed using standard methods from the literature. Prior to the analyses, soil water extracts (1:5, soil:water), were centrifuged at 32570 G for 15 min and passed through 0.45-µm Schleicher and Schuell syringe filter. The filtered solutions were analyzed using inductively coupled plasma emission spectroscopy (ICP-AES, spectro flame modula, spectroanalytical instruments GMBH, Germany) for cations and anions. The detailed procedure for the estimation of aqua-regia extractable Cr and total Cr(VI) are described in Section 3.2.3 and data is presented in Table 3.3 of Chapter 3. Soil solution Cr(VI) was analysed using Method 7199 developed by U.S. EPA (USEPA, 1996) for the determination of Cr(VI) in drinking water, ground water and industrial wastewater effluents by ion chromatography (DIONEX, Model 4000i, California, USA). Cr(III) concentrations in solution were derived from the difference between total Cr estimated by FAAS or GFAAS and Cr(VI) estimated by ion chromatography. The scanning electron micrograph and EDAX spectra of the surface and subsurface soil is presented in Fig. 5.1 and 5.2 respectively. The detailed estimation procedure for SEM and energy dispersive X-ray analysis is described in Section 3.2.3 of Chapter 3.

5.2.3 Desorption Studies

Initially batch desorption experiments were conducted on the surface (0-15 cm) and subsurface (50-90 cm) soils to assess the kinetics of Cr release, and to determine a suitable water:soil ratio for detailed studies. Soil samples (2, 1, 0.5 and 0.3 g) were equilibrated at various solution:soil ratios (10:1, 20:1, 40:1, and 100:1) using an end-over-end shaker operating at 10 revolutions per minute at a constant temperature of 20 ±

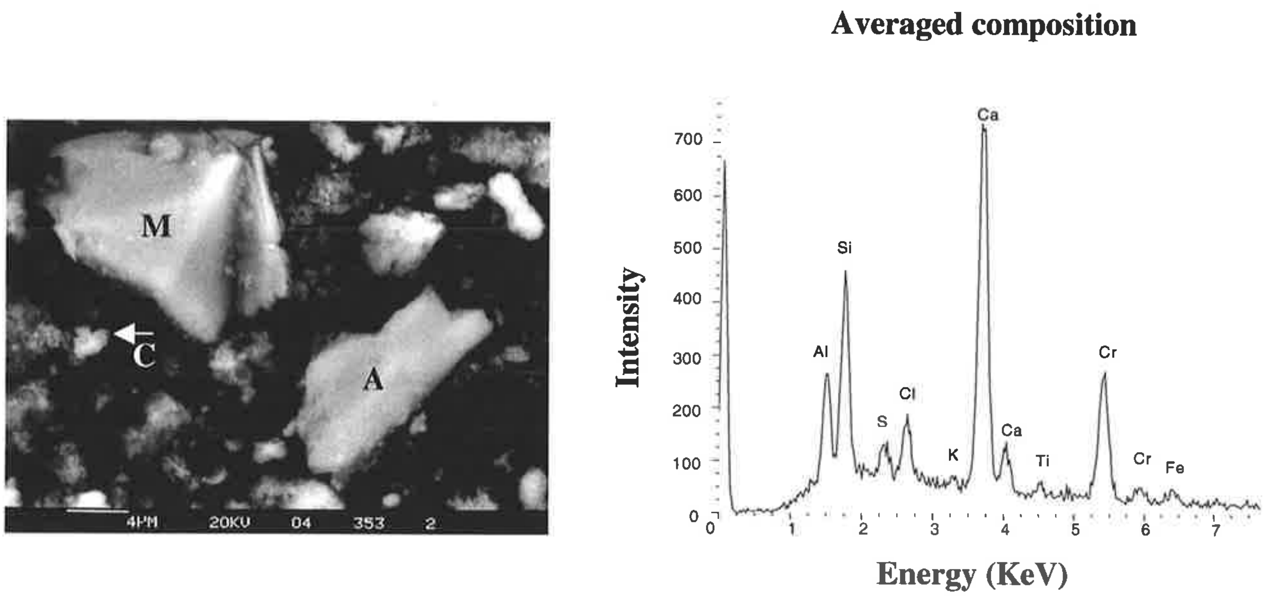


Fig. 5.1 Scanning electron micrograph of surface soil (0-15 cm) showing the presence of (M) magnesium silicate, (A) aluminum silicate and (C) calcite. The adjacent EDX spectra shows the averaged composition of the soil

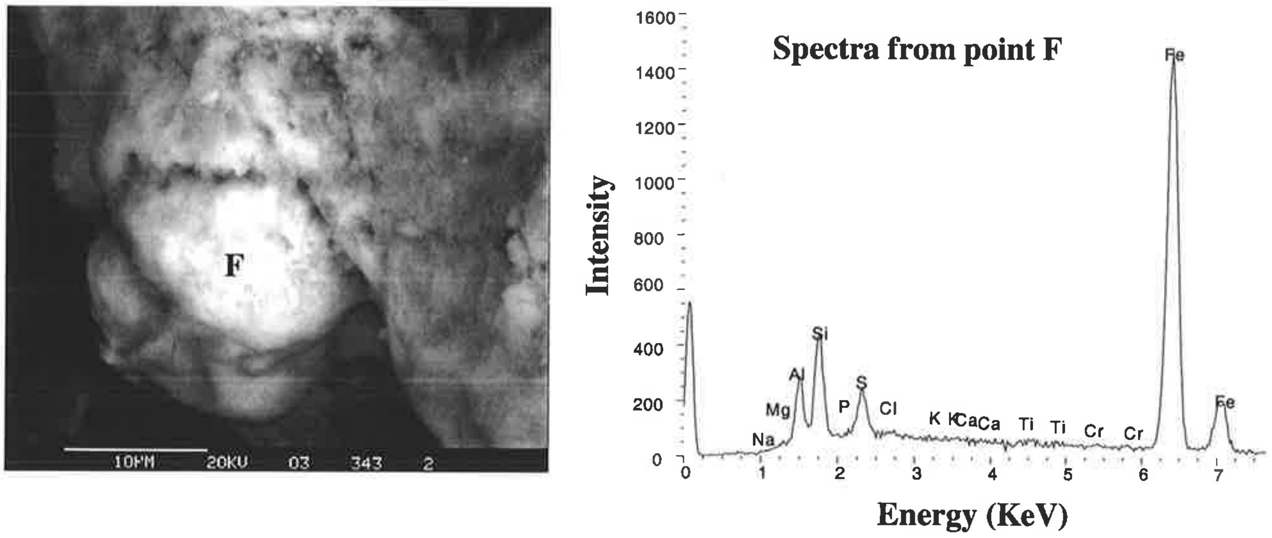


Fig. 5.2 Scanning electron micrograph of subsurface soil (50-90 cm) showing the presence of (F) highly weathered framboidal particles with morphology similar to pyrites. The adjacent spectrum was taken at point F

2 °C. Chromium release was studied at various equilibration times: 0, 0.08, 0.25, 0.50, 1, 2, 4, 8, 10, 24 and 48 h. Following equilibration, samples were centrifuged at 32570 G for 15 min and passed through 0.45-μm Schleicher and Schuell syringe filters to minimise colloidal contamination. Total Cr in the extracts was estimated by FAAS or GFAAS (APHA, 1992).

5.2.4 Kinetics of Cr Release

The kinetics of Cr release from contaminated soils was studied using a 20:1 solution:soil ratio for time periods ranging from 0 to 48 h. The soil solution ratio was chosen on the basis of the preliminary experiments described above. The samples were treated and analysed as described in Section 5.2.2 of this chapter.

5.2.5 Effect of Cations and P on Desorption of Chromium

The effect of cations, Ca^{2+} and Na^+ ($CaCl_2$, NaCl) and phosphate on desorption of Cr was investigated. While the ionic strength of the cation solutions was standardised at approximately 30 mmol/L, the concentration of phosphate (as KH_2PO_4) was varied from 0 to 3.2 mmol/L. MINTEQA2 speciation calculations show that at equilibrium the dominant phosphate species was $H_2PO_4^-$ in the pH range of 4.61 to 6.09. Samples of the contaminated soils (1.5 ± 0.01 g) were weighed into polypropylene centrifuge tubes. The total weight of tube and soil was recorded. The samples were then equilibrated with 30 mL of the electrolyte solution on an end-over-end shaker for 2 h at 20 ± 2°C. Following equilibration, the samples were centrifuged and filtered as described in Section 5.2.2. The filtered solutions were analysed for pH, Cr and the soluble cations and anions of interest following the methods described above. Between each equilibration, the centrifuged tubes containing the soil residues were weighed to account for entrained solution. The samples were then successively extracted four times with the appropriate electrolyte solution. All desorption experiments were duplicated.

5.3 Results and Discussion

5.3.1 Soil properties

The pH of the soil samples ranged from 7.9 in the surface 50 cm to 3.9 in samples below 50 cm depth (Table 5.1). The strongly acidic nature of soils below 50 cm is surprising because such an increase in soil acidity with depth has not previously been reported in duplex soils around Adelaide. Generally, duplex soils are typified by a loamy and acidic surface horizon overlaying a dense sodic ($pH > 7$) layer (Northcote and Skene, 1972). Detailed examination of the mineralogy of the soil using both XRD and SEM revealed the presence of large amounts of poorly ordered clay minerals (66%), calcite (15%), kaolinite (11%) and quartz (8%) in the surface soil samples (Fig. 5.1 and Table 3.5 of Chapter 3). The samples also contained large amounts of organic carbon (Table 3.3 of Chapter 3). The presence of calcite was expected because lime is used during the leather manufacturing process. Occasional iron-rich colloid particles with weathered surfaces were also evident from the SEM study. In contrast to the surface samples, the XRD traces of the subsurface acidic soil revealed the dominance of kaolinite (62%) and quartz (38%) (Table 3.5 of Chapter 3). Detailed SEM examination of these samples revealed highly weathered framboidal particles with morphology similar to that of pyrites (Fig. 5.2). It is likely that the strongly acidic nature of the subsurface soil is due to the weathering of pyrites (Eqn 1) during which SO_4^{2-} and H^+ ions are released. Such weathering reactions have been demonstrated to lead to increased acidity of the soils (Stevenson, 1986):

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1)$$

The aqua-regia extractable Cr concentrations are very high in the contaminated soil and varied with depth, ranging from 62 g/kg in the surface to 0.26 g/kg in the subsurface soil (Table 3.1 of Chapter 3). However, significant Cr(VI) concentrations present in the soil water extracts (0.27 – 0.43 mg/L) exceeded the Australian guidelines for drinking water set by the National Health and Medical Research Council (NHMRC, 1996) and guidelines of the United States Environmental Protection Agency (USEPA, 1991) for groundwater quality (0.05 mg Cr(VI)/L. The mobility of Cr(VI) at high pH is consistent with Naidu et al., (2000b) who reported high concentrations of Cr(VI) exceeding USEPA permissible limits in subsurface water samples, although these investigators did not determine the reasons for the high mobility of Cr at the site.

5.3.2 Desorption Studies

The solution (water):soil ratio had a significant effect on the amount of Cr desorbed. The effect of the solution:soil ratio varied with the pH of the soil. In the highly contaminated surface soil with high pH, increasing the solution:soil ratio led to an appreciable increase in the amount of Cr in solution (Fig. 5.3a).

This was expected because the desorption experiments were carried out under batch conditions and there was a greater sink for soluble Cr with increasing solution:soil ratio. However, in the strongly acidic (pH 3.9) subsurface soil the amount of Cr in solution decreased with increasing solution:soil ratio (Fig. 5.3a). The increasing solution:soil ratio was accompanied with an increase in soil pH to 4.4, which would

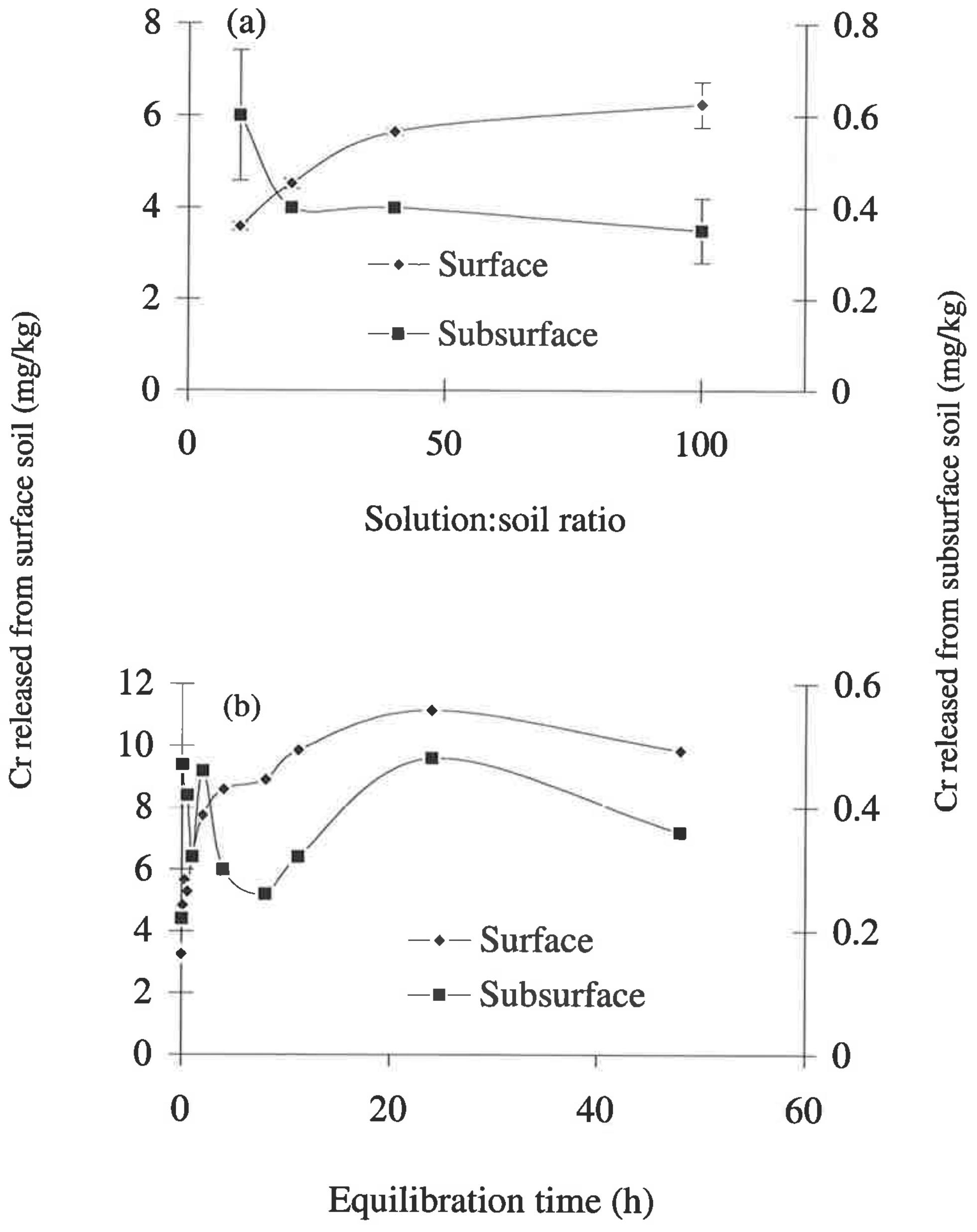


Fig. 5.3 (a) Amount of Cr released at various solution (water):soil ratios from surface and subsurface soil and (b) amount of Cr desorbed at different equilibration time from surface and subsurface soil. Bars represent standard deviation of the replicates

have favoured hydrolysis of Cr(III) to $Cr(OH)^{2+}$ or enhanced the soils capacity to adsorb the Cr(III) thereby decreasing the total Cr in solution. Speciation of soluble Cr in the soil water extracts showed that Cr(VI) was the predominant species in the surface alkaline soil, whereas Cr(III) was the predominant species in the subsurface acidic soil water extracts.

The amount of Cr desorbed increased with increasing time of contact in the surface soil . The maximum amount of Cr release was observed after 24 h. However, 80% of the total desorbable Cr was desorbed within 2 h (Fig. 5.3b). Considerably less Cr was released from the subsurface soil and the solution Cr concentration did not appreciably vary with equilibration time except within the first 10 h. The variations in desorbed Cr up to the 10 h equilibration time could be attributed to the strongly acidic pH of the soils (3.9), the solubility of Cr(III) and displacement and re-adsorption of exchangeable Cr(III) to competing cations in the batch system. The decrease in Cr release in both surface and subsurface soil solutions at 48 h of equilibration may be attributed to Cr re-adsorption over the long period of equilibration in the batch system. Given that 80% of the desorbable Cr was released within 2 h of equilibration of the surface and subsurface soils, we opted to conduct all sequential desorption studies for 2 h duration per equilibration.

5.3.3 Desorption of Cr in Water

With successive equilibrations, the cumulative Cr release increased in the alkaline surface soil. Considerably less Cr was desorbed from the acid subsoil, and most of the desorbed Cr was released in the first extraction (Fig. 5.4). Chromium speciation shows that all the desorbed Cr from the alkaline surface soil was present as Cr(VI) whereas all of the Cr in the acidic subsurface soil was present as Cr(III). At pH 3.9, the solubility of Cr(III) would be higher and only when the pH exceeds 5.5 does the solubility decrease because of the formation of Cr hydroxy complexes (Bartlett and Kimble, 1976a). These results are consistent with the intact core studies reported by Kookana et al., (2000), who demonstrated a similar pattern in Cr desorption from their column studies and those of James (1994) who also reported similar Cr release patterns from alkaline soils.

Although, the surface soil contained more than 62 g/kg Cr, only 5.12 mg/kg was desorbed into water in the first step of desorption (Fig. 5.4). Nonetheless, the Cr(VI) concentration (0.26 mg/L) in the first extract was more than 5 times the USEPA and NHMRC permissible concentrations for clean water. The continued slow release of Cr(VI) in successive water extracts, in excess of 10% of the total Cr(VI) present in soil, indicates the potential for the slow but continued loading of subsurface soils with Cr in percolating water at the contaminated site.

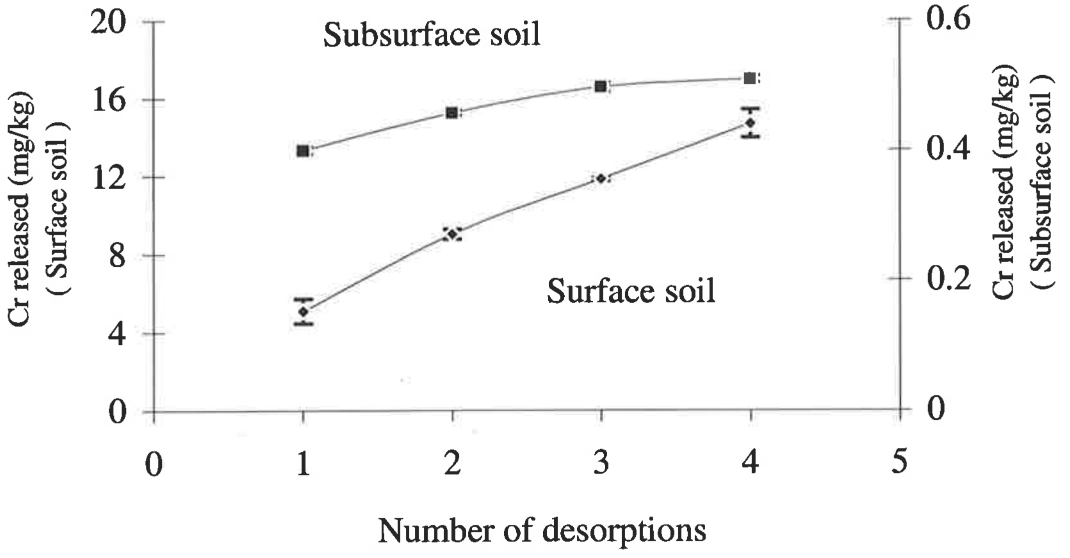


Fig. 5.4 Cumulative amount of Cr released in water from surface and subsurface soil. Bars represent standard deviation of replicates. Where no error bar is visible the error is smaller than the symbol. The scales are different for surface and subsurface soils

5.3.4 Effect of Cations on Cr Desorption

5.3.4.1 Surface Soil

The Cr(VI) concentrations desorbed from contaminated soils varied considerably with both the cationic charge of the added electrolyte and with various properties of the soil. In the surface alkaline soil, the Cr concentrations released decreased in the order: $Na^+ \geq$ water > Ca^{2+} (Fig. 5.5a). Leaching the surface soil with Ca^{2+} decreased the release of Cr(VI).

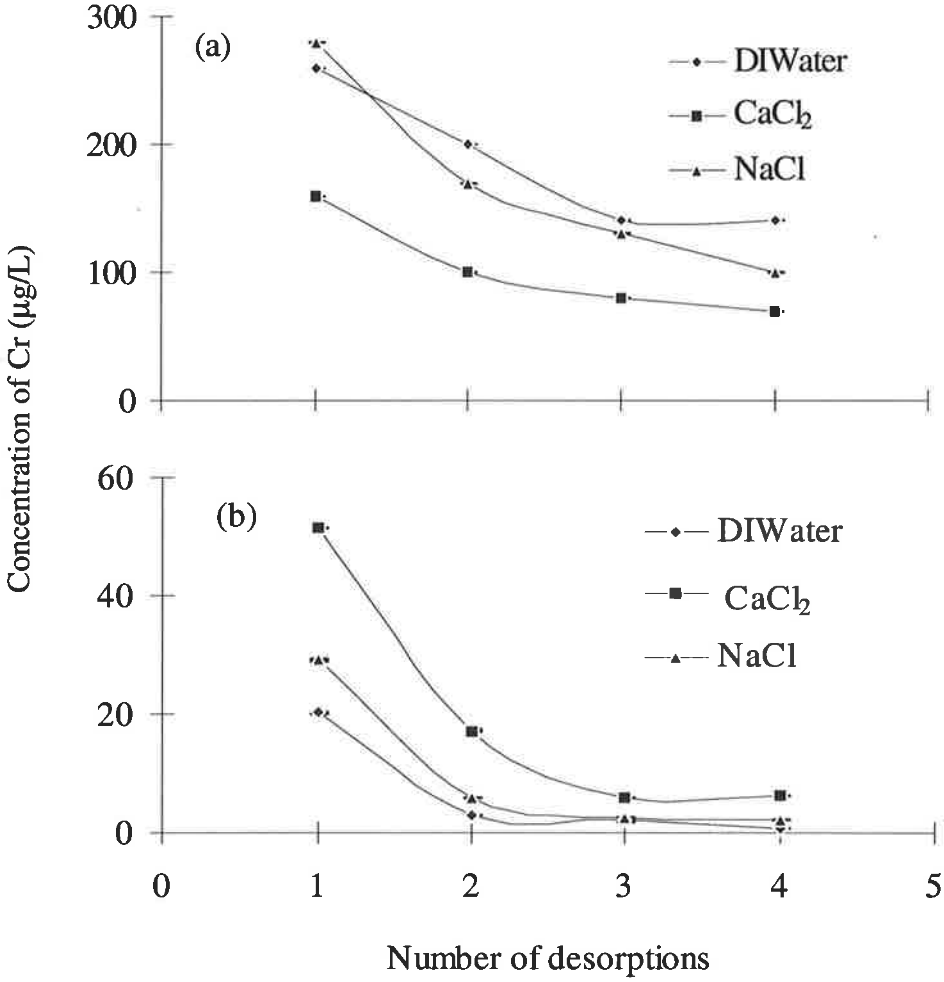


Fig. 5.5 Concentrations of Cr in distilled water, 0.01 M $CaCl_2$, and 0.03 M NaCl after repeated desorptions from (a) surface and (b) subsurface soil. Bars represent standard deviation of replicates. Where no error bar is visible the error is smaller than the symbol

The observed decrease of 0.3 to 0.5 pH units in the soil suspension when Cr was desorbed with Ca^{2+}, compared to Na^{+}, might have enhanced the retention of CrO_4^{2-} or $HCrO_4^{-}$ on to the soil. A decrease in soil pH would reduce the thickness of the double layer, which would enhance adsorption of the negatively charged Cr(VI) species, the dominant Cr species in the extract. Such a mechanism has been reported for anion adsorption studies by several investigators (Barrow, 1972 and Parfitt, 1978). As has been observed for iron oxide (Davis and Leckie, 1980; Zachara et al., 1987) and Al oxide (Aide and Cummings, 1997), bichromate ($HCrO_4^{-}$) is more strongly adsorbed and the dominant surface species that accounts for much of the increase in adsorption with decreasing pH. The decrease in Cr(VI) desorption in the presence of Ca^{2+} may be attributed to either the decrease in pH and/or to the changes in the thickness of the diffuse double layer and possibly the reduction of Cr(VI) to Cr(III) under high organic and ~~reduced~~ decreased pH conditions.

5.3.4.2 Subsurface Soil

The Cr release trend was reversed (i.e. $Ca^{2+} > Na^{+} >$ water) in the subsurface acidic soil compared to the alkaline surface soil. The Cr concentrations decreased gradually in subsequent desorptions (Fig. 5.5b). Speciation studies revealed the presence of only Cr(III) in the extracts, suggesting that the mobile Cr(VI) in the surface horizon is either adsorbed or transformed to Cr(III) in the strongly acidic subsurface soil. This may explain the absence of Cr in the fourth water extract. It is likely that Cr(III) is held tightly through covalent bonds and its displacement is difficult in water extracts (Drljaca et al., 1992). The release of Cr(III) in the Ca^{2+} and Na^{+} extracts may be through cation exchange, the divalent Ca^{2+} being more effective than monovalent Na^{+}.

Also Cr(III) has a tendency to hydrolyse and spontaneously form polynuclear complexes containing OH^- bridges. These forms of cationic Cr may be more susceptible to Ca^{2+} competition than Cr(III) itself, because they are larger cations where the charge is more evenly dispersed. While studying the effect of index cations on adsorption of Cd^{2+} by soils, Naidu et al., (1994) reported that divalent cations such as Ca^{2+} decreased adsorption of heavy metals. They attributed the decrease to a decrease in pH, compression of the double layer, and to increased competition for adsorption sites. Such a mechanism may be operative in the acidic subsurface soil in which Cr(III) is the predominant Cr species in the extract.

The proportion of Cr released in the first water extract relative to the total soil Cr varied from 4×10^{-4} % of the total Cr in the surface soils to 9×10^{-4} % of the total Cr in the subsurface soils. This suggested that the majority of the Cr present in these soils was insoluble and likely immobile. The results show that although the amount of total Cr exceeds 62 g/kg in the surface soils, the actual labile fraction is relatively low. Nevertheless, the concentration of Cr in the soil extracts exceeded the safe limits for clean water, and therefore, there is a concern of potential subsurface contamination of soil and ground water at the site.

5.3.5 Effect of Phosphate on Cr Desorption

Phosphate at concentrations > 1.6 mmol/L, increased the amount of Cr(VI) desorbed from surface soil. This effect was enhanced more in the presence of Na^+ than Ca^{2+} (Fig. 5.6 a and b). Since both chromate and phosphate are adsorbed by similar specific

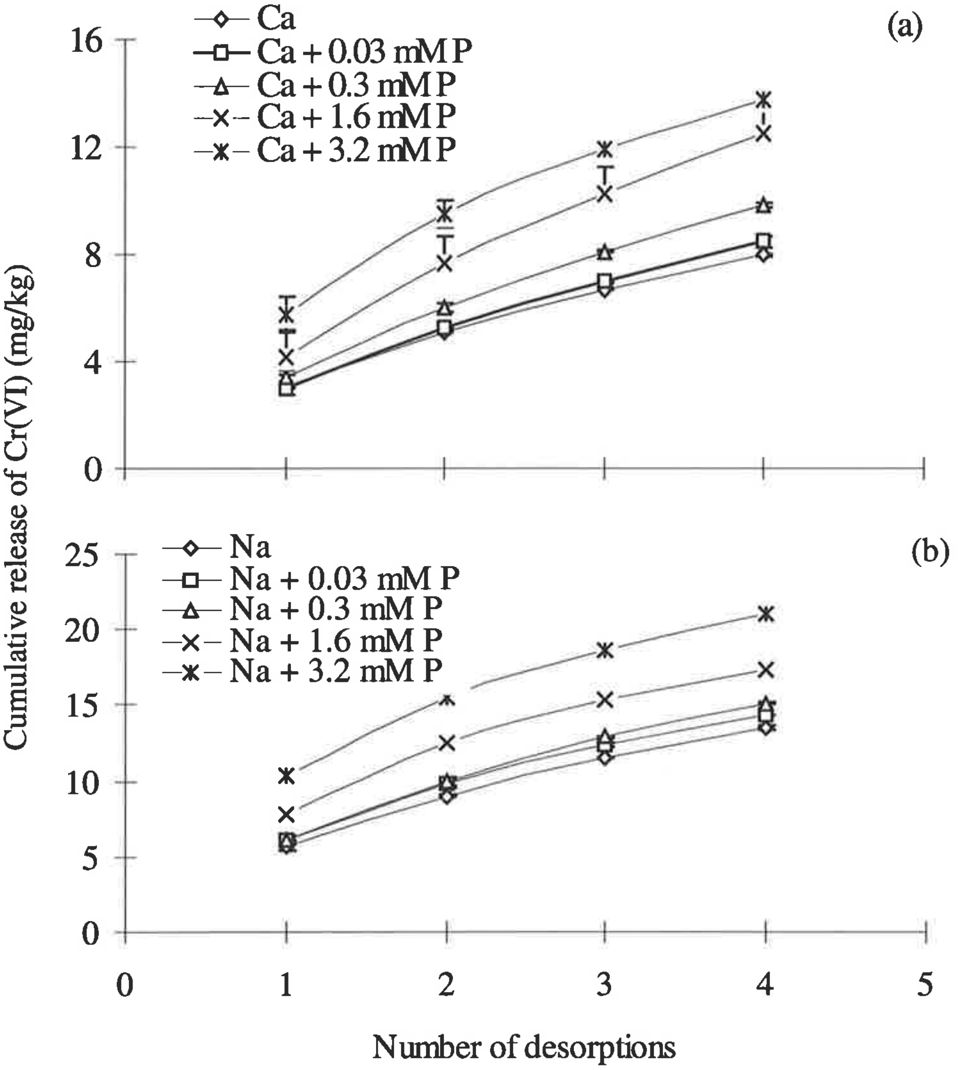


Fig. 5.6 Effect of index cations Ca (a) and Na (b) and P on the cumulative release of Cr(VI) from surface soil. Bars represent standard deviation of replicates. Where no error bar is visible the error is smaller than the symbol

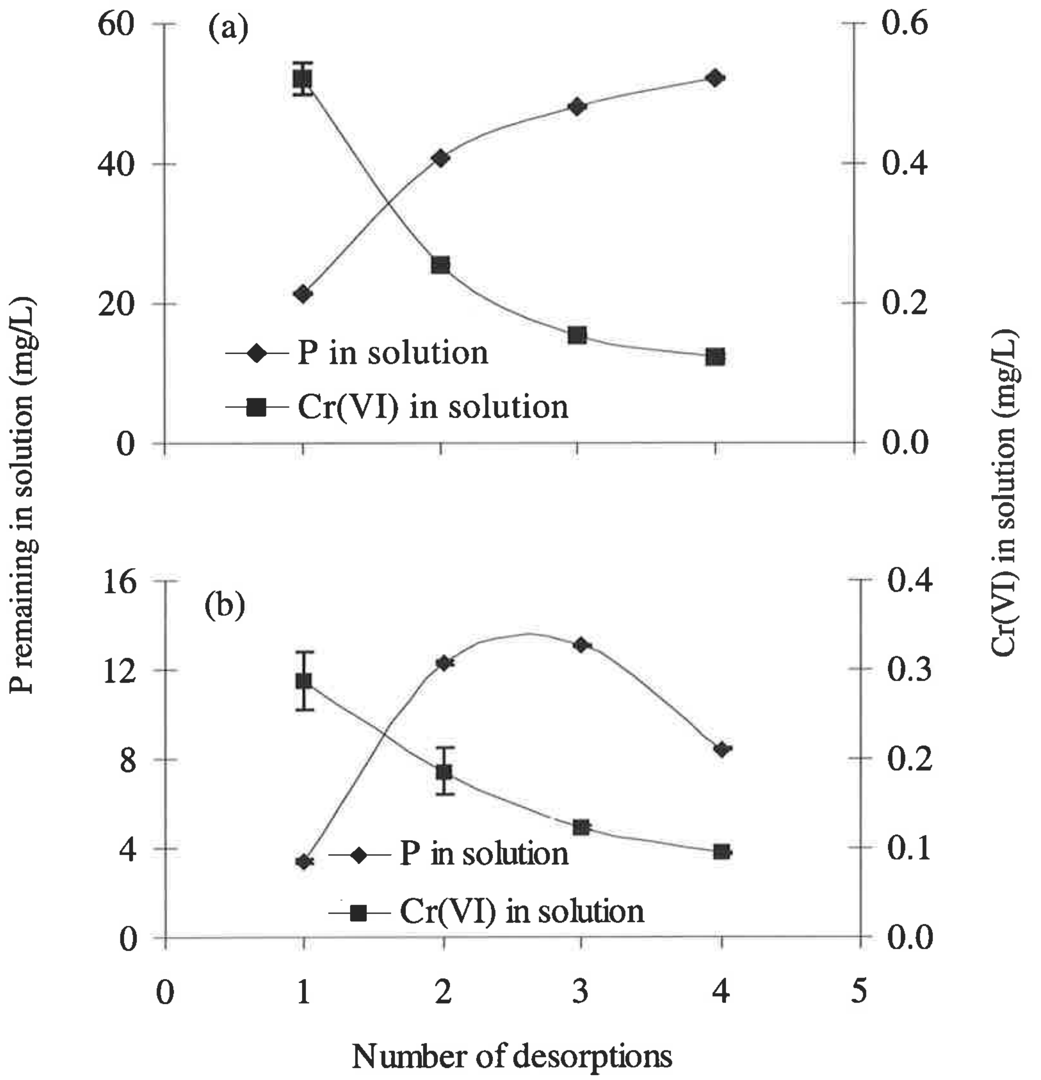


Fig. 5.7 Competitive release of chromate with 3.2 mM of P (the highest concentration of P used in the study in (a) Na and (b) Ca background electrolytes. Bars represent standard deviation of replicates. Where no error bar is visible the error is smaller than the symbol

adsorption mechanisms (Bartlett and James, 1988), the effect of Ca and Na on Cr(VI) desorption was expected. The amount of Cr(VI) desorbed by phosphate was always much higher in the presence of Na^+, compared to Ca^{2+} (Fig. 5.6a and b).

The concentration of Cr(VI) decreased progressively with each subsequent desorption and P concentration in the soil suspension increased with increasing number of desorptions in the presence of Na^+ which clearly indicates the competitive nature of the HPO_4^{2-} ion for CrO_4^{2-} adsorbed sites (Fig. 5.7a). This trend was not observed with phosphate in the presence of Ca^{2+} (Fig. 5.7b). This may be due to the decreased activity of phosphate through the formation of the aqueous $CaH_2PO_4^+$ species. MINTEQA2 (Allison et al., 1990) speciation of the equilibrium solution estimated that $CaHPO_4$ contained 33.2% of the P and $CaH_2PO_4^+$ contained 4.5% of the P in the Ca^{2+} system as compared to 15% $CaHPO_4$ and 2% $CaPO_4^-$ in Na^+ system.

Phosphate at a concentration of 3.2 mmol/L in both electrolytes desorbed nearly 85% more Cr(VI) compared with the phosphate free system, and a significant correlation of phosphate adsorption and chromate desorption was observed in the contaminated surface soil (Fig. 5.8).

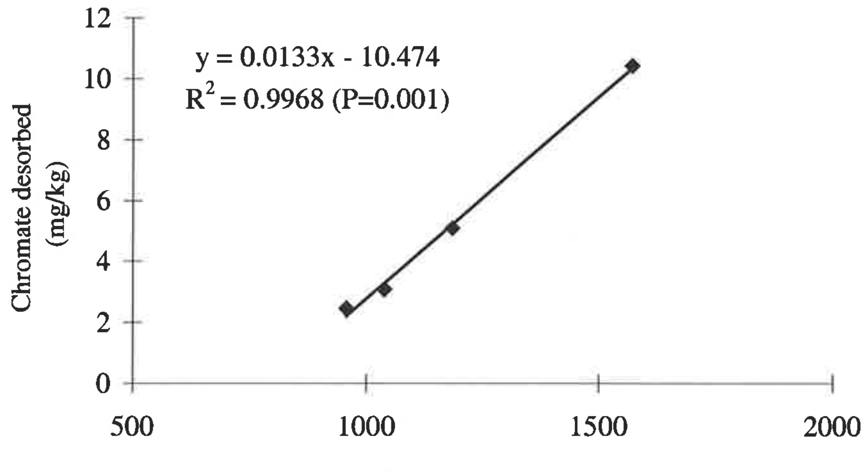


Fig. 5.8 Linear relationship between phosphate adsorbed and chromate released in the contaminated surface soil using 3.2 mM phosphate in a Na background

5.4 Conclusions

Based on the above study, the following conclusions were drawn.

- The observed trends in the release of Cr from these surface and subsurface soil indicates the importance of different oxidation states of Cr and the nature of their release in the desorption process.
- The initially rapid and subsequently slow release of Cr(VI) in an excess of over 10% of the total Cr(VI) present in soil to water extracts of surface soil samples from the contaminated site (pH 7.9) illustrated the potential for the slow but continued loading of subsurface soil and subsequently the groundwater resources with Cr from percolating water. In contrast to the surface soil, release of < 0.2% of the total Cr in the acidic subsurface soil (pH 3.9) was not significance in the potential migration of Cr.
- In the selected "hot-spot" at the contaminated site, the presence of an acidic subsurface horizon might have favoured adsorption of Cr(VI) and reduction of Cr(VI) to Cr(III).
- In the surface alkaline soil, Cr release decreased with increasing cationic charge (water $\geq Na^+ > Ca^{2+}$) while the trend was reversed ($Ca^{2+} > Na^+ >$ water) in the acidic subsurface soil.
- Compared to the Na^+ system in alkaline soil the presence of Ca^{2+} favoured greater retention and lesser mobility of Cr(VI). In acid soils cationic competition may desorb and facilitate migration of Cr(III). Both pH and nature of Cr appear to play a significant role in the desorption process in the presence of electrolytes.
- The competitive effect of phosphate, in both cationic background solutions on desorption of Cr(VI) from the surface soil of the contaminated site was significant.

However, the release of Cr(VI) was enhanced at higher phosphate concentrations (>3.2 mmol/L) in the solution.

CHAPTER 6

Retention and Release of Chromium in Soil Contaminated with Tannery Waste – Column Leaching Studies

6.1 Introduction

In the previous chapter the effects of added electrolytes on Cr desorption was studied in a batch system. These studies enabled us to identify the major factors (aqueous) that influenced Cr desorption in the tannery waste contaminated soils. However, batch techniques represented a close system since the desorbed species are not removed from the sorbing environment and products are allowed to accumulate in the system. The retained reaction products may influence desorption processes and their interpretation because (a) reactions may not be unidirectional and reverse reactions are often not considered, and (b) desorbed species may cause secondary reactions – for example, precipitation (Sparks, 1989; Amacher et al., 1990). On the other hand, release of the reaction products may better reproduce field conditions, because surface reactions normally occur in micropores or within relative static surface films in the macropores. Mixing rates of soil and solution can also greatly affect results (Ogwada and Sparks, 1986). If mixing rates are too slow, reaction interpretation is confounded by diffusion reactions and conversely if mixing rates are too fast, new specific surface areas and sorption sites can be created due to abrasion as particles collide in suspension. In a review of methods used for investigating contaminant-soil interactions, Harter and Naidu (2001) concluded that considerable caution must be exercised while relating batch data to processes that occur in soil. For these reasons, we investigated desorption of Cr from a long-term contaminated soil using a repacked column. The desorption solution varied in the nature of index cations (Na^+, Ca^{2+}) and anions ($H_2PO_4^-$). These cations and anions were used because they were typically the major cations and anions present in tannery effluents. These ions were also the predominant species present in the soil pore water at the contaminated site (Naidu et al., 2000a). Column leaching studies were thought to provide a more realistic indication of the amount of labile Cr present in the contaminated soil. The specific objectives were:

(1) To investigate the effect of solution Ca^{2+} and Na^+ on the retention and release of Cr(VI) from contaminated surface soil in a column leaching system, and

(2) To study the competitive effect of $H_2PO_4^-$ on release of Cr(VI) from the contaminated surface soil in a column leaching system.

6.2 Materials and Methods

Soil samples were collected from the surface (0-15 cm) of the soil profile excavated at the long-term tannery contaminated site at Mount Barker, South Australia. Detailed information on the contaminated site and soil physiochemical properties is presented in Chapter 3, Table 3.3 and 3.4. Soil was oven dried at 40°C, crushed by pounding in a machine fitted with rubber rollers, passed through a 2 mm stainless steel sieve and stored in polyethylene containers. The stored soil was thoroughly mixed before it was packed into a glass column (20 x 1.6 cm, Amersham Pharmacia Biotech AB, Uppsala, Sweden) for column leaching studies. Pertinent properties of the soil are presented in Table 6.1.

The column was packed by adding small amounts of soil (calculated to obtain the desired bulk density in a 0-15 cm layer in the column) and tapping in order to attain uniform packing devoid of pathways that would facilitate preferential flow. A high flow

Table 6.1 Physicochemical characteristics of the soil used for the study

Depth (cm)	pH	EC (dS/m)	Total Cr (mg/kg)	Total Cr(VI) (mg/kg)	Organic carbon (g/kg)	Ca (mg/kg)	Na (mg/kg)	Fe (mg/kg)	S (mg/kg)
0 -15	7.94	0.67	61785	40	101.2	2470	652	6539	7509

Table 6.2 Details of the electrolytes used in column leaching experiments

Electrolytes and sequence of leaching	Solution pH	Pore Volume (ml)	Bulk density (g/cm^3)
1. Deionised water	6.37	26.53	0.68
2. Deionised water + 3 mmol KH_2PO_4/ L	4.92	26.30	0.70
3. 10 mmol/L $CaCl_2$ followed by 30 mmol/L NaCl	5.73 & 5.73	26.60	0.68
4. 30 mmol/L NaCl followed by 10 mmol/L $CaCl_2$	5.82 & 5.73	26.47	0.70

rate of 0.5 ml/~~day~~ min was used to remove the column eluent as quickly as possible in order to minimise adsorption of the metal either by test tubes in which the fractions were collected and also to minimise the potential for any other atmospheric chemical reaction. A peristaltic pump delivered solutions into the column. The soil column was leached with electrolytes against gravity in order to avoid entrainment of air in pore spaces. The pore volume and bulk density of the soil are presented in Table 6.2.

6.2.1 Electrolyte Concentrations

Ca^{2+}, Na^+, Cl^- and $H_2PO_4^-$ were the electrolytes leached through the contaminated soil. Whereas the ionic strength of the solutions of Ca^{2+}, Na^+ and Cl^- was maintained at 30 mmol/L, the concentration of P was 3.2 mmol/L as a result of batch desorption studies conducted on the same contaminated soils. Reagent-grade chemicals $CaCl_2$, NaCl and KH_2PO_4 were used to prepare the various influent solutions. Fresh solutions were prepared for each leaching experiment which was performed by packing a new batch of contaminated soil into the dry glass column after completely removing the soils leached previously and thoroughly rinsing the glass column, nylon filters, plastic distribution plates and flow tube accessories. Details of the sequence and type of leaching experiments are given in Table 6.2.

6.2.2 Pore Volume

The pore volume was calculated from the gravimetric moisture content measured after saturating the dry soil column. The glass column with all accessories and packed with dry soil was weighed before saturating the soil column with water at the desired flow rate. Immediately after flow was observed at the eluent-end of the soil column the flow was stopped and the column, including saturated soil and accessories was reweighed. The gravimetric water content and pore volumes were then calculated from the difference in weights of dry and saturated columns.

6.2.3 Leaching Sequence and Effluent Collection

The soil column was saturated with deionised water before leaching with electrolyte solutions. The soil column was leached with deionised water and deionised water + 3 mmol P/L separately by repacking the glass column with contaminated soil each time. In the case of 10 mmol/L $CaCl_2$ followed by 30 mmol/L NaCl, 22 pore volumes of $CaCl_2$ were leached followed by NaCl. Leaching fractions were collected in acid washed test tubes of 15 mL capacity in a fraction collector programmed to collect 0.5 pore volumes per tube. Prior to analysis, two fractions were mixed to form one pore volume, passed through 0.45 μm syringe filters, and stored in acid washed polypropylene containers prior to chemical analysis. Two leaching sequences were carried out: Ca^{2+} followed by Na^+ after 22 pore volumes and Na^+ followed by Ca^{2+} after 11 pore volumes.

6.2.4 Calcium Effect on Cr(VI) – Batch Desorption

The effect of Ca^{2+} at various concentrations on the release behavior of Cr(VI) from the contaminated surface soil was investigated using short batch desorption experiments to test our hypothesis. Contaminated soil (1.5 g) and $CaCl_2$ solution (30 ml) was transferred to a polyethylene screw cap container and equilibrated for 2 h on an end-over-end shaker operating at 10 revolutions per minute at a constant temperature of 20 ± 2 °C. The suspension was centrifuged at 15,000 rpm (32570 g) for 20 minutes, filtered through 0.45 μm syringe filters and stored in a polypropylene container for analysis of total Cr and Cr(VI). The procedure was carried out in duplicate. The concentrations of $CaCl_2$ solutions were 0.001 M, 0.002 M, 0.003 M, 0.01 M and 0.05 M.

6.2.5 Analytical Methods for Aqueous Total Cr and Cr(VI)

All extracts were analysed for pH, total Cr and Cr(VI) immediately following collection and filtration of fractions (0.45 μm syringe filters) prior to acidification and storage at $4^{o}C$ in the cold room for further analysis. After measuring the pH of leachates, total Cr in the leachates were analysed by flame atomic absorption spectroscopy (FAAS) and, in the samples where aqueous Cr concentrations were <0.1 mg/L, by graphite furnace atomic absorption spectrometry (GFAAS) (APHA, 1992). Hexavalent Cr was analysed by ion chromatography using an anion exchange column (USEPA, 1996). Ca, Na, P and S were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Detailed analytical procedures are described in Chapter 3, Sections 3.2.1 and 3.2.3.

6.3 Results and Discussion

6.3.1 Chromium Release from Contaminated Soil

The contaminated soil column leached with deionised water showed an initial release of 0.7 mg/L of Cr in the first pore volume (PV) and a slight increase in concentration for the second PV (Fig. 6.1). A gradual decrease in the concentration of Cr released was observed from the third PV to 24 PV at which point the column run was stopped. All the Cr released from the contaminated soil was present as Cr(VI) and no

Cr(III) was released. A total of 9.21 mg/kg of Cr(VI) was released in 24 PV out of a possible total of 40 mg/kg of Cr(VI) present in the contaminated soil. At the start of leaching, the pH of deionised water was 6.37 but this increased to 7.78 in the first PV and continued to increase until it stabilised at 8.2 after 12 PV.

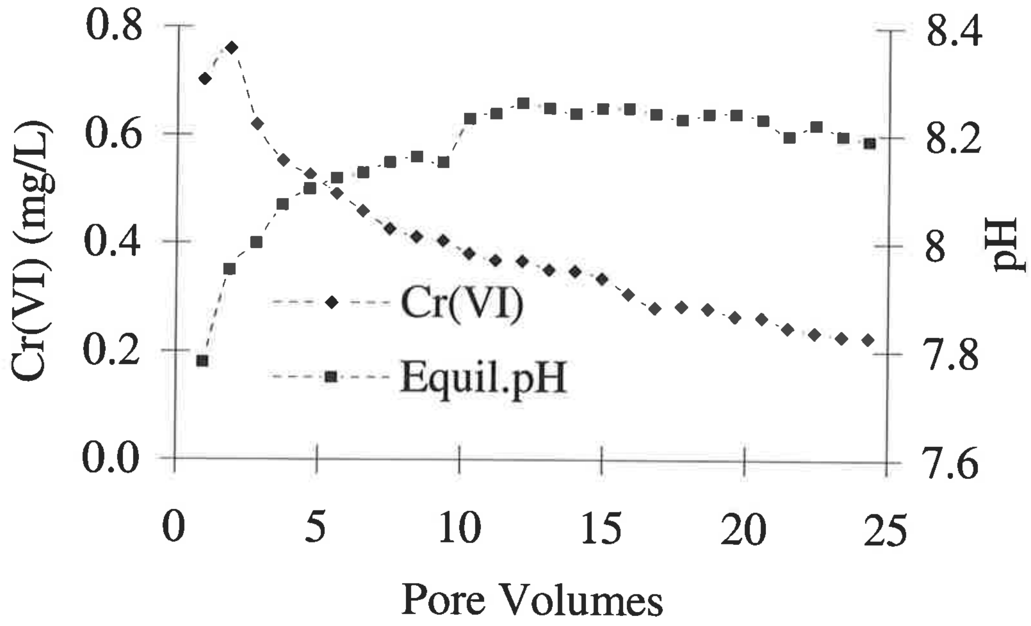


Fig. 6.1 Effluent Cr concentration and pH in column experiment using deionised water

The ready desorption of Cr was not surprising given the presence of Cr(VI) in the contaminated surface soils (Avudainayagam et al., 2001). It was expected that the alkaline soil pH would inhibit anion adsorption especially in soils with high net negative surface charge. The conditions of high soil pH (>7.94) together with low anion exchange capacity of the contaminated soil appear to enhance chromate release into soil solution (Parfitt, 1978; James and Bartlett, 1983c). These results are consistent with earlier reports (Kookana et al., 2000; James, 1994; Weng et al., 1994) on Cr(VI) mobility in high pH contaminated soils. Even though the contaminated surface soil had 40 mg/kg of total Cr(VI), the rate of chromate release slowed after the first PV.

Thermodynamically the dominant chromate species present in high pH soils would be expected to be CrO_4^{2-}. Its association with other salts in the soil determines the solubility of Cr(VI) in solution. In the soil used in this experiment, Cr(VI) may have been associated with moderately soluble $CaCrO_4$ and this may have been the reason for the continued slow release of Cr(VI) through out the run (Nieboer and Jusys, 1988). Nearly 9 mg Cr(VI)/kg soil was desorbed during the run of 24 PV. The trend in Cr release suggests the continued release of Cr(VI) had the leaching continued for more than 24 PV. The concentration of Cr(VI) released was also significantly higher (0.3 mg/L) than the maximum permissible level for Cr(VI) in natural water. The slow release of Cr(VI) in water extracts indicated the potential for continued leaching of subsurface soils with Cr(VI) in percolating water at the contaminated site.

6.3.2 Effect of Ca^{2+} and Na^+ on Cr Leaching

~~Contrary to~~ Compared to leaching with deionised water, leaching of the soil column with $CaCl_2$ led to a marked decrease in the amount of Cr released in the eluent for the first 4 PV (Fig. 6.2). Subsequent leaching of the soils showed a gradual decline in Cr. The initial release of Cr(VI) in the first PV was similar to the release of Cr(VI) with deionised water. However, in the subsequent pore volumes the concentrations of Cr(VI) released decreased significantly reaching 0.3 mg/L in the fifth PV and attaining a steady release of 0.2 mg/L from 10 PV (Fig. 6.2). However, when Ca was replaced with Na, the amount of Cr desorbed increased with each additional PV of the electrolyte reaching a maximum of 0.36 mg/ L at 28 PV. Thereafter the Cr gradually decreased to 0.23 mg L^{-1} at 42 PV when the run was stopped.

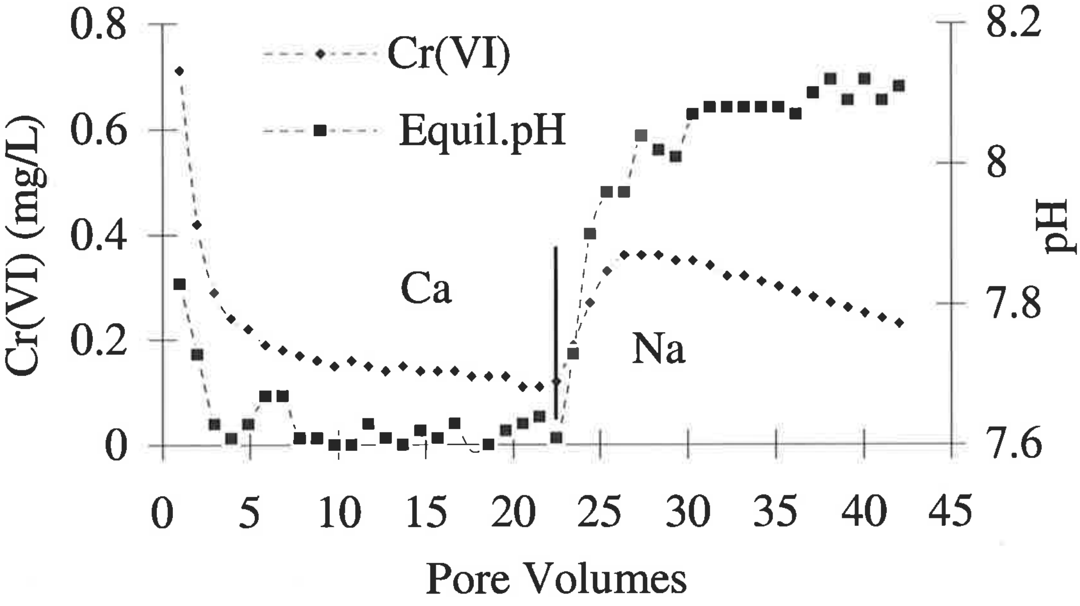


Fig. 6.2 Effluent Cr concentration and pH under $CaCl_2$ conditions followed by NaCl introduced after the 20th pore volume

The decrease in the release of Cr(VI) in the presence of Ca^{2+} may be attributed to (a) enhanced adsorption of Cr(VI) following a reduction in surface negative charge as a result of specific adsorption of Ca^{2+} on the ion exchange sites (Barrow, 1972) and (b) enhanced adsorption of Cr(VI) as a result of a decrease in soil pH (Fig. 6.2). Our observation of the effect of Ca on solution pH and enhanced Cr adsorption is supported by Zachara et al., (1987) who found that the introduction of Ca^{2+} decreased soil pH by reducing net negative charge in the double layer which enhanced electrostatic retention of CrO_4^{2-}. This effect of Ca^{2+} on CrO_4^{2-} was observed in the presence of cations at pH > 7. This effect was particularly marked in the presence of divalent cations, although monovalent cations such as K^+ also induced greater retention with the effect varying with the selectivity for sorption on particulate surfaces (Davis and Leckie, 1978; Balistrieri and Murray, 1982). According to Zachara et al., (1987), divalent cations such as Ca^{2+} may also increase CrO_4^{2-} adsorption in high pH soils presumably by forming Ca^{2+}-CrO_4^{2-} ion pairs and subsequent adsorption on surfaces (S) as shown by the following equation;

$$SOH + H^+ + Ca^{2+} + CrO_4^{2-} \Leftrightarrow SOH_2^+\text{-}CrO_4Ca^o$$

When NaCl was introduced into the soil column that was originally leached with Ca^{2+} (at 23 PV), the concentration of Cr(VI) in the eluent increased from 0.2 mg/L to 0.36 mg/L after an equilibration time of one pore volume (at 24 PV). The increase in the release of Cr(VI) corresponded to a sharp increase in the equilibration pH of leachates (Fig. 6.2). After the initial increase, Cr(VI) in the eluent started to decrease from 30 PV and reached the steady release of 0.2 mg/L at 43 PV at which point the run was stopped.

The above column study was repeated but with NaCl as the first influent solution followed by $CaCl_2$. There was an enhanced release of Cr(VI) in the Na^+ leachings and it continued with each PV up to the introduction of Ca^{2+} (Fig. 6.3).

The enhanced release of Cr(VI) coincided with an increase in the equilibration solution pH. After the introduction of Ca^{2+} at 10 PV, it took nearly three pore volumes to equilibrate the soils with Ca^{2+} and thereafter the concentration of Cr(VI) in the effluent dropped significantly to 0.25 mg/L at 13 PV and to <0.1 mg/L at 15 PV. The trend in retention of Cr(VI) in the presence of Ca^{2+} was similar to the observations in our batch desorption studies using the same contaminated soils (Avudainayagam et al., 2001). There is another possibility viz. that CrO_4^{2-} might have precipitated as $CaCrO_4$

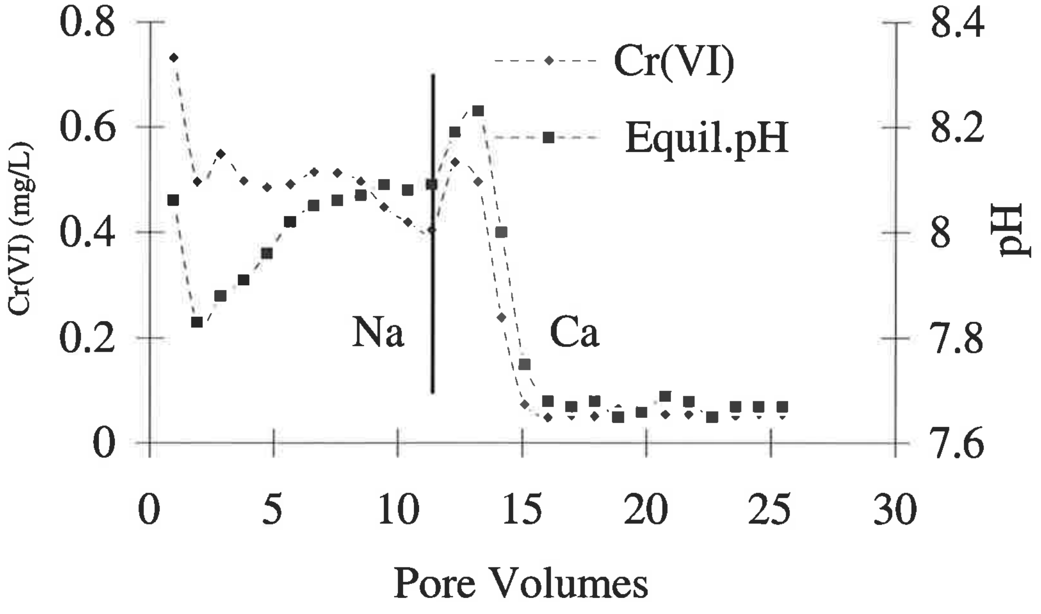


Fig. 6.3 Effluent Cr concentration and pH under NaCl conditions followed by $CaCl_2$ introduced after the 10th pore volume

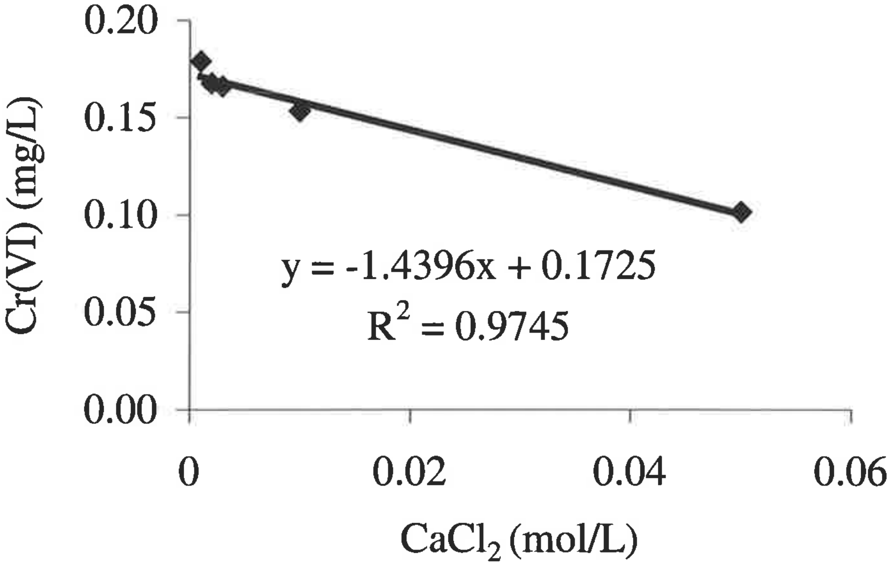


Fig 6.4 Concentration of Cr(VI) desorbed from a long-term contaminated surface soil as a function of $CaCl_2$ concentration

because of the excess Ca^{2+} added to the contaminated soil which already had higher amounts of Ca^{2+} than normal soils. However, MINTEQA2 speciation of the effluent of the first five pore volumes during the Ca^{2+} leachings did not predict any precipitation of $CaCrO_4$.

6.3.3 Calcium Effect on Cr(VI) Leaching

From the batch desorption results we observed that there was a significant decrease in desorption of Cr(VI) as the concentration of Ca^{2+} was increased (Fig. 6.4). This again indicated that the presence of Ca^{2+} in soil solution favoured higher retention of Cr(VI) in the contaminated soil environment. We conclude that application of divalent cations to Cr-contaminated soils could help in reducing the mobility of Cr, a possible remediation option for Cr-contaminated soils.

6.3.4 Effect of Phosphate

The effect of P on Cr release varied significantly between the first to 9th pore volumes of influent solution. A Cr concentration of 0.68 mg/L was observed in the first PV leachate when the column was leached with deionised water containing 3 mmol/L of P (Fig. 6.5). After a slight increase in concentration at 2 PV, Cr concentrations continued to decrease up to 5 PV and increased to almost 0.7 mg/L at 9 PV. Thereafter Cr release decreased gradually to 0.37 mg/L at 21 PV when the column run was stopped. The continuous release of 0.37 mg/L of Cr even after 21 PV of leaching demonstrates the presence of a significant labile (bioavailable) fraction in these contaminated soils. Speciation of Cr in these leachates showed that all the desorbed Cr in the leachate was in the Cr(VI) form. The pH of the leachate increased to 7.87 in the first PV from the influent solution pH of 4.92. A continued increase in the leachate pH was observed for subsequent pore volumes and reached a pH of >8.50 at 21 PV (Fig. 6.5).

Comparison of Cr(VI) in the effluent solutions in the presence and absence of P shows similar concentrations up to 5 PV. Continued leaching of soils beyond 5 PV showed ~~significantly~~ substantially higher concentrations of Cr(VI) in the presence of P compared to leaching with deionised water alone (Fig. 6.6).

Enhanced release of Cr(VI) in the presence of P suggests the presence of appreciable concentrations of exchangeable fractions of Cr(VI) as reported in Chapter 4. Enhanced release of Cr(VI) in the presence of P is not surprising given the similar chemistry of these two (P and Cr(VI)) ligand ions. The phosphate and chromate anions would compete for adsorption sites i.e. these anions inhibit the adsorption or promote desorption of each other (Bartlett and James, 1988; and Stollenwerk and Grove, 1985). However, in the initial 5 pore volumes, phosphate might have been adsorbed non-specifically to the surface soil sites. The other possibility for the loss of phosphate in solution could be the formation of a Ca-P ion pair or even precipitation as amorphous calcium phosphate (ACP). The data on Ca^{2+} release from contaminated soil shows (Fig. 6.7) that in the first five PV the concentration of Ca^{2+} ranged from 101-362 mg/L which might have favoured the formation of Ca-P ion pairs or precipitation of ACP. MINTEQA2 speciation of the effluent from the first pore volume predicted 51.6 % of phosphate species bound as $CaHPO_4$, 10.4 % as $CaPO_4^-$ and 32.6 % bound as HPO_4^{2-} confirming decreased phosphate activity in the solution when the Ca^{2+} concentration was 362 mg/L. At 5 PV, when the Ca^{2+} concentration was 101 mg/L, the MINTEQA2 predicted an increase in the P species, HPO_4^{2-} from 32.6 % to 52.4 % and a corresponding decrease in the $CaHPO_4^-$ bound species from 51.6 % to 31.8 %.

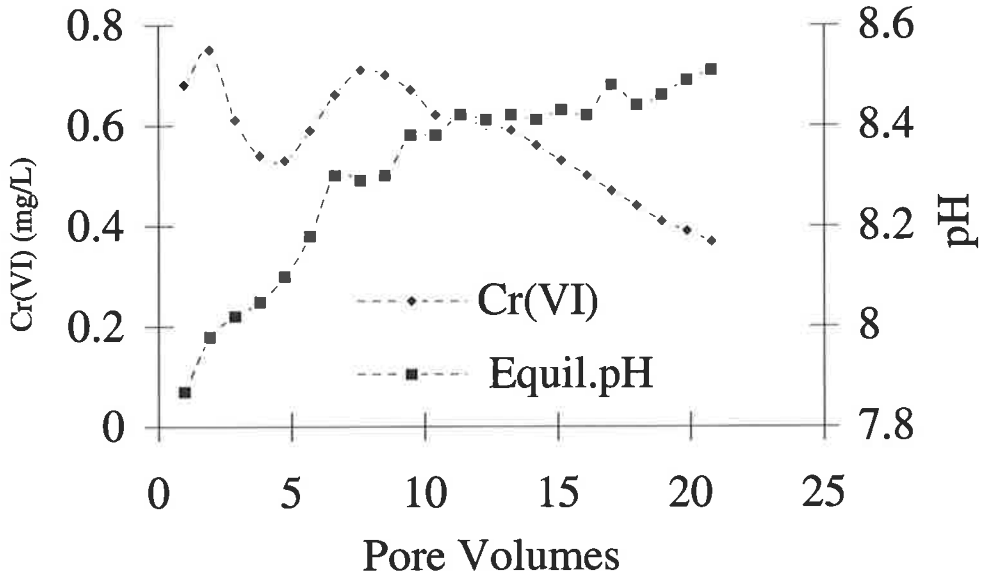


Fig. 6.5 Effect of P (3.2 mmol/L) on effluent Cr and pH

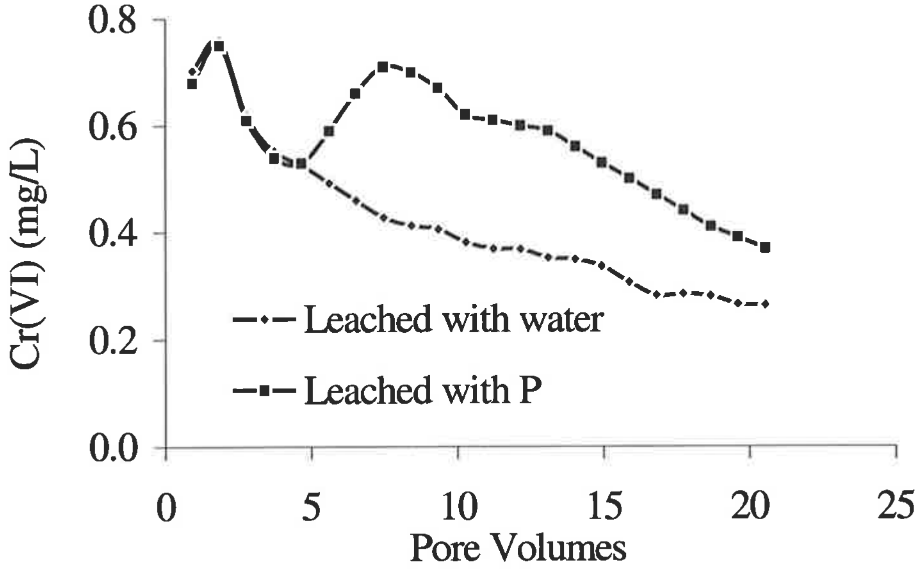


Fig. 6.6 Enhanced leaching of chromate with 3.2 mmol phosphate compared to water

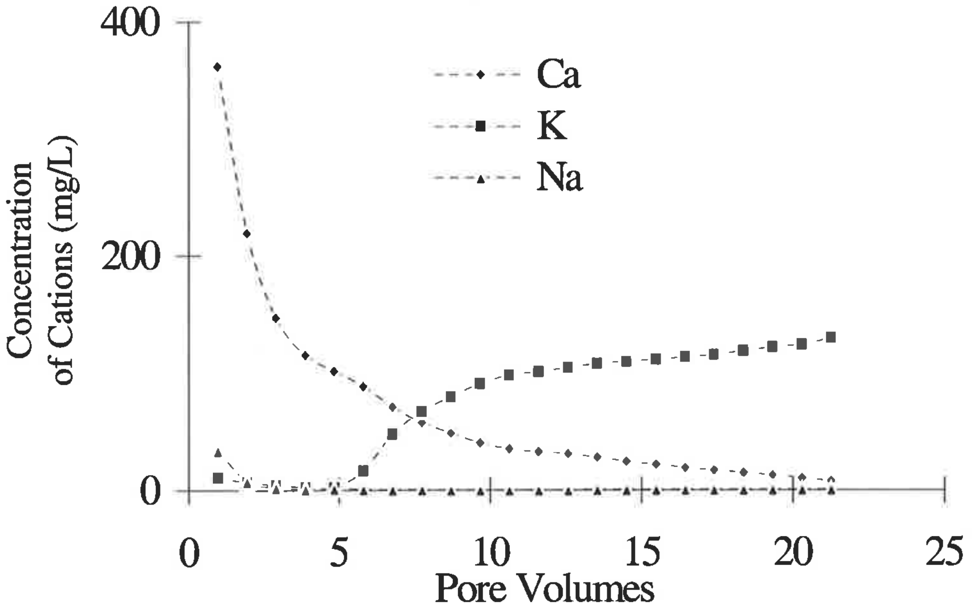


Fig. 6.7 Concentration of cations in the leachate during phosphate leaching of the contaminated soil column

Many investigators have studied the precipitation of calcium phosphate in solution and have observed that the ionic activity product (IAP) for the ACP formed in alkaline conditions, e.g. pH 7.4 - 9.3, was relatively constant with starting Ca/PO_4 molar ratio of 1.31 to 1.48 and stoichiometry of the solids of $Ca_3(PO_4)_{1.87}(HPO_4)_{0.2}$ (Van Kemenade and De Bruyn, 1987; House 1989, and Eanes, 1998). In our experiments, the Ca/P ratio was 3.3 and, based on our observations, it is likely that all calcium-phosphate phases, namely dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP), tricalcium phosphate (TCP) and calcium hydroxyapatite (HAP) could be forming at this ratio. Therefore pecipitation or ion pair formation might have decreased the ionic activity of phosphate in the solution for competitive release of Cr(VI) during the first five pore volumes. Once the Ca^{2+} concentrations in solution decreased there may have been increased desorption of Cr(VI) facilitated by the presence of more free phosphate ions in solution.

The results of the cumulative release of Cr(VI) with deionised water and phosphate showed that the presence of phosphate enhanced the release of Cr(VI) from the contaminated surface soil. For the same 21 pore volumes, an increase of 2.4 mg/kg of Cr(VI) was observed in the presence of phosphate in the leaching solution. The data on anion P in the leachates showed that most of the applied P was sorbed or precipitated to the soil and some of it could have displaced S from the soil site (Fig. 6.8).

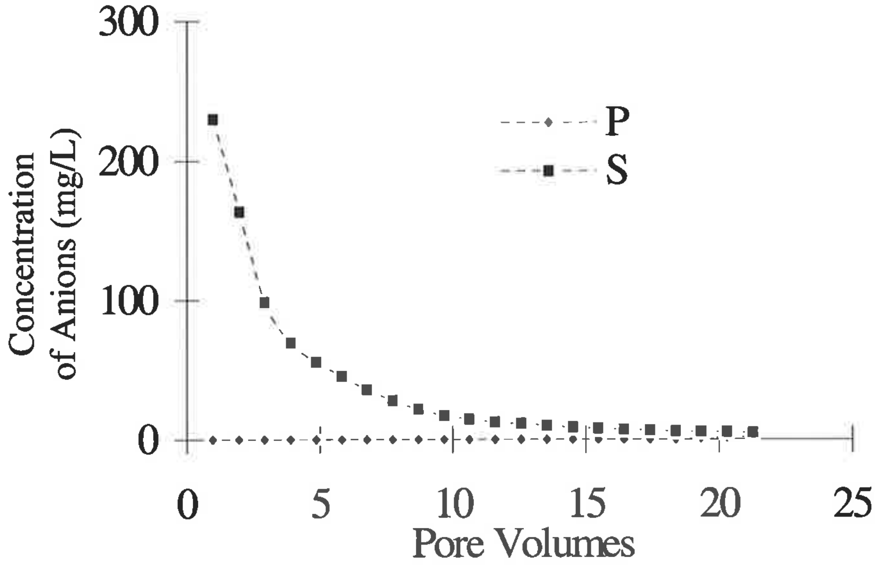


Fig. 6.8 Concentrations of anions in the leachate during phosphate leaching of the contaminated soil column

6.3.5 Effect of Electrolytes on Cr(VI) Desorption – A Comparative Study

All the electrolytes showed varied effects on desorption of Cr(VI) from contaminated soil (Fig. 6.9). Among the cations, Na^+ showed similar desorption trends to that of deionised water. However, there was a marked decrease in the amount of desorbed Cr(VI) in the presence of Ca^{2+}. When the column was leached with the Ca-P solution, the concentration of Cr(VI) released in the first 5 PV was similar to that desorbed in deionised water. The lack of the effect of P on Cr(VI) desorption in the

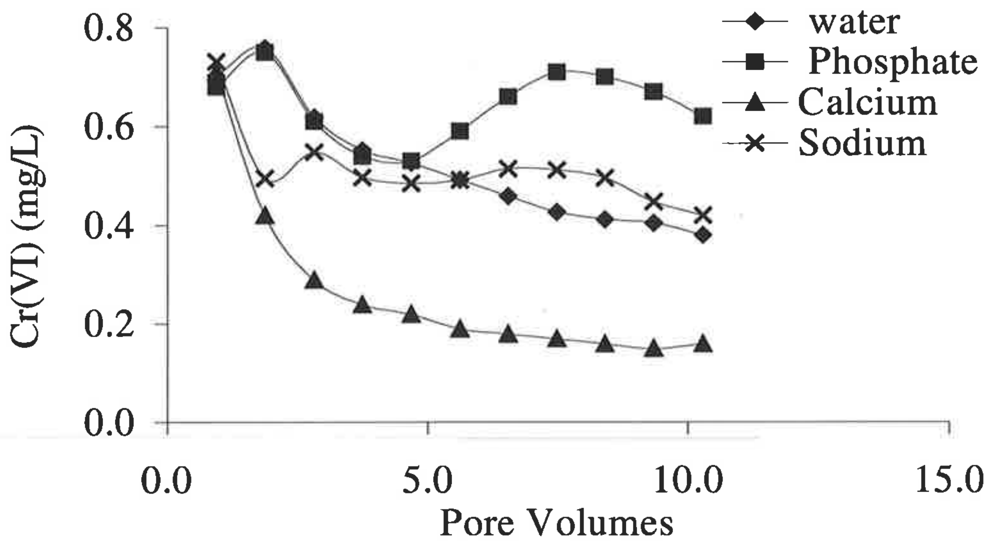


Fig. 6.9 Effect of electrolytes on leaching of Cr(VI) from the contaminated soil

Table 6.3 Proportion of P in leachate solution as influenced by presence of Ca

Pore Volume	Species (%) MINTEQA2	
	$CaHPO_4$	HPO_4^{2}
1	51.6	32.6
5	31.8	52.4

presence of Ca^{2+} during initial desorption may be attributed to the possible formation of $CaHPO_4$ thereby reducing the activity of $H_2PO_4^-$ for competitive anion exchange with CrO_4^{2-} and $HCrO_4^-$. This is also supported by data on Ca concentration that shows a marked decline with each PV of influent solution (Fig. 6.7). Low concentration of Ca^{2+} beyond 5 PV will increase the activity of $H_2PO_4^-$ in the effluent solution leading to increased desorption of Cr(VI) through anion exchange. This was supported by MINTEQA2 speciation calculations that predicted that the percentage of HPO_4^{2-} (52.4%) was more in leachate solution at 5 PV than at 1 PV (Table 6.3).

6.4 Conclusions

From the results discussed in this chapter the following conclusions were drawn,

- In tannery waste contaminated alkaline soil, weakly bound CrO_4^{2-} was readily leached by all of the electrolytes considered in this study.
- The significant increase in leaching of Cr(VI) by Na^+ was attributed to an increase in soil pH favouring leaching of the anion CrO_4^{2-}. In both leaching situations Ca^{2+} decreased the soil pH and might have induced adsorption of CrO_4^{2-}. This suggests that if Ca^{2+} dominates the solution composition in a contaminated soil it may suppress the release of Cr(VI) or favour adsorption of Cr(VI) on to surface sites.
- From the results of this study we conclude that application of divalent cations, especially Ca^{2+}, will retard migration of toxic Cr(VI) to subsurface and prevent contamination of groundwater aquifers in chromate contaminated sites. Further studies are needed to develop options for remediating chromate-contaminated soils.

- The enhanced release of Cr(VI) in the presence of phosphate ligands at concentrations >3.0 mmol/L was confirmed and at the same time the presence of Ca^{2+} at saturated concentrations in a tannery contaminated soils induced the formation of calcium-phosphate phases and decreased the ionic activity of phosphate.

CHAPTER 7

In-situ Stabilization of Chromate in Tannery Waste Contaminated Soils: Preliminary Studies

7.1 Introduction

Both solid phase speciation (Chapter 4) and laboratory column studies (Chapter 6) demonstrated the presence of labile (water soluble and exchangeable) Cr(VI) in soils at the Mount Barker contaminated site. The total area of the contaminated site is nearly 7 ha. However, almost 90% of the site is disturbed and the concentration of Cr in the disturbed soils ranged from <50 mg/kg to over 500 mg/kg. In contrast to the disturbed soils, the undisturbed site is highly contaminated with the concentration of total Cr exceeding 9% in the surface soils (Chapter 4). In the highly contaminated site soluble Cr(VI) in the piezometeric water was sometimes reported to exceed 0.35 mg Cr(VI)/L at a depth of 50 cm (Naidu et al., 2000a). The presence of Cr(VI) in piezometric water samples together with evidence of Cr(VI) in ground water (Naidu et al., 2000a) prompted us to develop strategies for managing the contaminated sites. Such strategies include (a) excavation and transport of the contaminated soil to appropriate landfill sites and (b) chemical immobilization of Cr(VI). If the excavation and transport to landfill option were to be adopted then the remediators would be faced with the removal of nearly 2800 t of contaminated soil. This is an impractical and uneconomical approach. Moreover, the recent NEPC-ACS (NEPC, 1999) guidelines do not permit transfer of highly contaminated soils to landfill sites. For this reason *in-situ* stabilization appears to be the best alternative remediation strategy. *In-situ* remediation generally involves removal of contaminants from the soil or immobilization of contaminants that leads to a reduction in bioavailability. For metal contaminated soils both onsite soil washing

(Naidu et al., 2000a) and electrokinetic remediation techniques have been used at selected sites. However, neither of the two technologies is popular with the remediation industry due to the high costs and the long period required for remediation. In contrast to these techniques, chemical immobilization of metals is being considered as an attractive option. This technique does not remove metals from the site but immobilises them irreversibly. The low cost associated with the technology makes this an attractive option.

Because Cr undergoes transformation between toxic Cr(VI) and relatively non toxic, immobile Cr(III) species in soils, the first step in the *in-situ* stabilization would be to reduce the toxic Cr(VI) to non toxic Cr(III) species. Although this alleviates the hazard imposed by Cr(VI), the possibility of reoxidation of Cr(III) to Cr(VI) needs consideration. Organic matter, Fe(II) and sulphides are capable of reducing Cr(VI) (Makos and Hrncir, 1995; Elovitz and Fish, 1995; Wittbrodt and Palmer, 1995; Saleh et al., 1989; Ishibashi et al.,1990). The organic reductants of Cr(VI) may form soluble chelated complexes with Cr(III) which may enhance the potential for re-oxidation to Cr(VI) by MnO_2 (James and Bartlett, 1983a and b). However, inorganic reductants, such as Fe(II), eliminate this possibility by promoting the formation of Cr(III) solids of low solubility (Sass and Rai, 1987). Moreover, the formation of a solid Cr(III) phase greatly diminishes the potential for transformation back to Cr(VI) (Fendorf et al., 1992).

Although organic matter has been shown to be an effective reductant for Cr(VI) (James, 1994), it was surprising to note that even the presence of 10% organic carbon in the soil of the contaminated site was not effective in the complete reduction of soluble Cr(VI). The presence of Cr(VI) may be attributed to two competing reactions: (i) the reduction of Cr(VI) by organic matter and (ii) oxidation of Cr(III) in the presence of Mn(IV). The prevailing reaction will dictate the end product.

Even after twenty five years of tannery waste disposal significant amounts of total and soluble Cr(VI) was found in the contaminated site. One possible reason for this may be a low microbial load or sparse microbial diversity due to the presence of toxic Cr(VI) which may have decreased the rate of organic matter mineralization in the contaminated soil. The other possibility may be the presence of 244 mg/kg of aqua-regia extractable Mn, most likely present as MnO_2, which would favor oxidation of organically reduced Cr(III).

Several studies have shown the effectiveness of Fe(II) in chromate reduction. Fe(II) was a major reductant of Cr(VI) in forested wet land soils (Masscheleyn et al., 1992). The rate of chromate reduction by Fe(II) was rapid and was found to proceed even in the presence of dissolved O_2 at $pH \leq 8.0$ (Fendorf and Li, 1996). James (1994) studied chromate reduction, in alkaline soils enriched with the processing residue of chromite ore, with various reductants and concluded that Fe(II) was more effective than Mn^{2+}, steel wool, hardwood tree leaf litter or lactic acid. However, studies using Fe(II) as a reducing agent mixed with soil and also observations of re-oxidation of reduced Cr(III) in a tannery waste contaminated soil have not been reported so far. Hence, the present study was conducted with the following objectives:

1) To optimize the dose of Fe(II) required to reduce water soluble and exchangeable Cr(VI) in this highly contaminated surface soil (0 –15 cm)
2) To investigate the stability of remediation technology under wet-dry cycles similar to those observed in the field; and
3) To investigate the potential of surface mixed Fe(II) to stabilise subsurface chromate in the contaminated soils.

7.2 Materials and Methods

The batch method was followed to optimize the amount of Fe(II) required to reduce the water soluble and exchangeable Cr(VI) present in the contaminated surface soil. A commercial grade $FeSO_4.7H_2O$ was used as the source of Fe(II) and was chosen considering practical applications to field conditions. The Fe(II) to Cr(VI) ratio was based on the soil weight used for the study. A kinetic experiment was carried out initially to investigate the rate of reduction of Cr(VI) by Fe(II) in the contaminated soil.

7.2.1 Kinetics of Cr(VI) Reduction

Air dried <2 mm surface soil (10 ± 0.01 g) was transferred to a pre-weighed 40 mL polyethylene centrifuge tube and the tube was reweighed after $FeSO_4$ addition (Table 7.1). The air-dried soil and $FeSO_4$ salt were equilibrated for 24 h by shaking in an end over end shaker. After equilibration, distilled water (20 mL) was added and the mixtures further equilibrated for increasing time intervals. The kinetics of Cr(VI) reduction by Fe(II) in the contaminated soil was studied using this mix system. The experiment was duplicated and two tubes were removed at time intervals of 0.5, 1, 5, 7, and 24 h. These tubes were centrifuged at 15,000 rpm (32570 G) for 15 minutes. The supernatant was passed through 0.45 μm syringe filters and stored in a polystyrene containers for pH, total Cr and Cr(VI) analysis. The tubes were weighed after decanting the supernatant to determine the residual solution and 20 ml of 10 mM phosphate buffer (K_2HPO_4/KH_2PO_4 – pH 7.2) was added to two replications for each Fe(II) treatment in order to extract exchangeable Cr(VI) from the soil plugs. After shaking for 18 h, the tubes were centrifuged and total Cr and Cr(VI) were determined in the filtered solutions.

Table 7.1 Treatments used for the kinetic experiments

Treatment	Percentage Fe(II) added
1. Control (contaminated soil alone)	0
2. 13.3 mg of $FeSO_4$	0.1
3. 26.6 mg of $FeSO_4$	0.2
4. 53.2 mg of $FeSO_4$	0.5
5. 1 g of $FeSO_4$	10

7.2.2 Iron Optimization for Chromate Reduction

In order to investigate the efficiency of Fe(II) and practicality of field applications, very high and low doses of Fe(II) were used in the kinetic experiments. ~~While~~ However, in this series of experiments to optimize the Fe(II) dose, for efficiency and practicality, different levels of Fe(II) were used (Table 7.2). Based on the results of the kinetic experiments an equilibration time of 24 h was selected for the optimization studies. Water soluble Cr and exchangeable Cr(VI) were extracted using methods similar to that described in the kinetic experimental section. As described previously, the pH, total Cr and Cr(VI) of the extracts were all measured. All treatments used in subsequent studies were conducted in duplicate. The solution:soil ratio and other equilibration procedures were the same as followed for the kinetics of Cr(VI) reduction experiment described in section 7.2.1, except instead of 10 g of air dried < 2mm soil contaminated soil, 5 g of soil was used here.

Table 7.2 Treatments used during Fe(II) optimization studies

Treatment	Percentage Fe(II) added
1. Control (contaminated soil alone)	0
2. 0.05 g of $FeSO_4$	1
3. 0.125 g of $FeSO_4$	2.5
4. 0.250 g of $FeSO_4$	5.0
5. 0.375 g of $FeSO_4$	7.5

7.2.3 Soil Moisture Conditions for Incubation Studies

The approximate field moisture capacity percentage was estimated for the <2 mm surface soil at 10 kPa (Cassel and Nielsen, 1986) and 50% field moisture capacity was maintained throughout the period of the experiment.

7.2.4 Incubation Studies

After ascertaining the efficiency of Fe(II) to reduce water soluble and exchangeable Cr(VI), 1% and 2.5% Fe(II) treatments were selected for the incubation experiment. Incubation studies were conducted in plastic pots by transferring 300 g of air-dried < 2 mm soil mixed with $FeSO_4$ and maintained at a particular field moisture capacity (50%). The $FeSO_4$ was mixed well with the dry soil and left for 24 h to equilibrate in the pots before addition of distilled water to maintain a 50% field moisture capacity. The pots were weighed at both dry and moist conditions (50% field moisture capacity). Pots were reweighed daily and distilled water added to maintain constant field moisture capacity. The treatments were performed in triplicate and included, control (contaminated surface soil alone), 3 g of $FeSO_4$ (1%), and 7.5 g of $FeSO_4$ (2.5%). The experiment was conducted in a glasshouse maintained at 20 ± 2 °C. The total period of the incubation study was 110 days.

7.2.5 Wet and Dry Cycles

In order to simulate field conditions and also to investigate the effect of wetting and drying on re-oxidation of Fe(II)-reduced Cr(III), wet and dry cycles were included in the incubation experiment. In the first 30 days 50% field moisture capacity was maintained for all treatment pots, during the next 55 days the pots were left to dry and for the remaining 25 days 50% field moisture capacity was again maintained. A complete dry period started nearly ten days after the first 30 days.

7.2.6 Soil Sampling and Sampling Intervals

Soil samples from incubated pots were collected at time intervals of 3 h and 1, 2, 14, 30, 85 and 110 days. Samples were collected from the surface after a thorough mixing of the soil using a plastic spatula. The samples were packed in 25 mL disposable syringes by tapping, where the syringe outlet had previously been packed with acid washed glass wool to prevent the loss of soil particles during centrifugation. A sample was collected after allowing one-hour equilibration for the water added to maintain the field moisture capacity. Uniform quantities of soil were collected from all the pots in such a way that it filled the syringe up to 20 – 25 mL mark. The pots were weighed after each sampling to help maintain the field moisture capacity.

7.2.7 Pore-water Collection

Soil pore-water was isolated by centrifugation as described by Gillman and Bell (1978). The pore-water was filtered directly through 0.45 µm syringe filters into polystyrene containers. The pH, total Cr and Cr(VI) in the pore water was determined immediately to ensure minimum changes in these parameters.

7.2.8 Exchangeable Cr(VI)

After pore-water was collected the same soil samples from each treatment were removed from the disposable syringe, air dried in a fan forced oven (40 °C) and extracted with phosphate buffer for measurement of exchangeable Cr(VI). The extraction method followed was same as that described above (Section 7.2.1). Exchangeable Cr(VI) was measured only once for each period of wet, dry and wet cycles.

7.2.9 Methods of Analysis

The pH was measured using an ORION pH meter, total Cr in the solution was determined using FAAS or GFAAS, Cr(VI) by ion chromatography and the difference between total Cr and Cr(VI) was considered to be Cr(III) in solution. The detailed estimation procedures were described in Chapter 3.

7.3 Results and Discussion

7.3.1 Parameter Optimisation for Optimum Cr(VI) Reduction

The following preliminary studies were conducted to estimate (a) an appropriate equilibration period, (b) moisture conditions and (c) Fe(II) levels for optimum reduction of Cr(VI).

7.3.1.1 Kinetics of Cr(VI) reduction by Fe(II)

Data presented in Fig. 7.1 confirms previously published reports that Fe(II) is an effective reductant of Cr(VI) (James, 1994). The amount of Cr(VI) reduced increases with increasing concentration of Fe(II) in the contaminated soil (Fig. 7.1.). However, in this study, data also shows that the amount of total soluble Cr increases with increasing duration of incubation, suggesting that for complete equilibration incubation periods exceeding 30 min may be needed. This would be especially relevant for soils with large pools of total and exchangeable Cr.

The result of the kinetic study showed that at any given time, Cr(VI) reduction was rapid and that increasing levels of Fe(II) increased the reduction of water-soluble Cr present in the soil. This effect of Fe(II) was also observed for exchangeable Cr(VI). Figure 7.1 clearly depicts a proportional decrease in the concentration of total Cr in solution with increasing Fe(II) dose mixed with the soil even within 30 min. However, the decrease in concentrations of Cr was most significant with increasing Fe(II) levels during the first 30 min of incubation compared to longer equilibration times. Among the Fe(II) treatments a significant reduction of total soluble Cr was observed for 0.5% and 10% of $FeSO_4$ treatment compared to the control at 30 min equilibration. The reduction

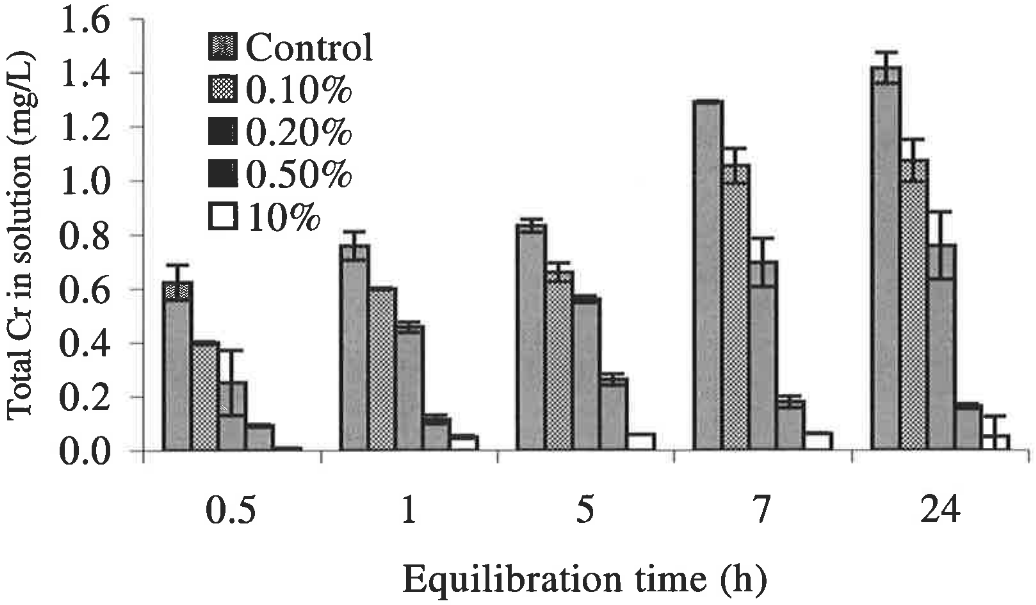


Fig. 7.1 Effect of equilibration time and Fe(II) levels on soluble Cr

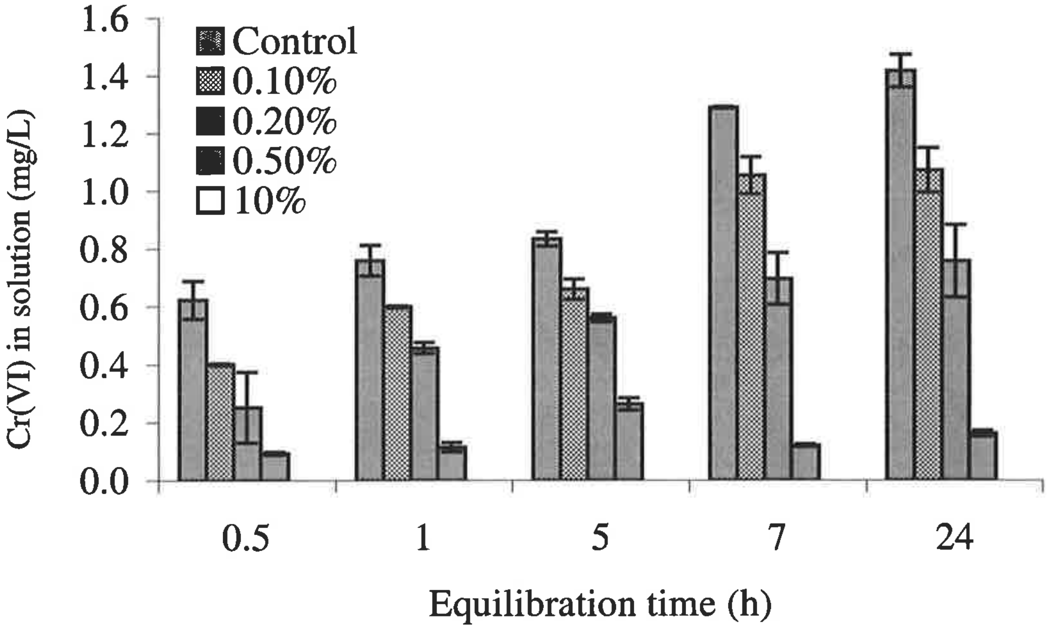


Fig. 7.2 Water soluble Cr(VI) reduction with increasing Fe(II) levels and equilibration time

of water-soluble Cr was nearly 85% and 100% for the 0.5% and 10% $FeSO_4$ treatments respectively. As observed during the Cr desorption kinetics study in Chapter 5 there was an increase in total soluble Cr concentrations with increasing equilibration time. This increase of total soluble Cr was obvious in the control, 0.1% and 0.2% $FeSO_4$ treatments. However, mixing high $FeSO_4$ did not show a definitive trend for total soluble Cr.

7.3.1.2 Aqueous Speciation of Cr

Aqueous speciation of Cr revealed Cr(VI) to be the dominant species in water extracts in most of the treated soils (Fig. 7.2). The dominance of Cr(VI) in the soil aqueous phase is not surprising given the high soil pH, which favours desorption of Cr(VI). In the column leaching studies described in Chapter 6 a similar Cr(VI) desorption trend was observed from the contaminated surface soil. Not surprisingly the extent of Cr(VI) reduction was dependent on $FeSO_4$ loading. Complete reduction of Cr(VI) was recorded at the highest dose of Fe(II) (10% $FeSO_4$), at all equilibration times commencing from 30 min. Speciation studies revealed that all water-soluble Cr in the 10% $FeSO_4$ amended soil was Cr(III). A significant reduction of Cr(VI) was also observed for the Fe(II) dose of 0.5% $FeSO_4$ compared to the control. With increasing equilibration time desorption of Cr(VI) increased in the control and in the first two levels of Fe(II) treatments. The application of 0.5% $FeSO_4$ did not show a definite trend in the desorption of Cr(VI) with increasing equilibration time.

According to Fendorf and Li, (1996) the reduction of Cr(VI) by Fe(II) is fast and they predicted that the reduction of 0.1 mM Cr(VI) in oxygenated solution by 0.3 mM

Fe(II), even at pH 8, would be complete within 0.5 min. Eary and Rai (1988) described the reduction of aqueous Cr(VI) by aqueous Fe(II) by the following equation;

$$\mathrm{Cr(VI)\ (aq) + 3Fe(II)\ (aq) \rightarrow Cr(III)\ (aq) + 3Fe(III)\ (aq)} \qquad \text{(Eq 7.1)}$$

The overall reaction was complete within 1 – 2 minutes. In the present study the shortest time observed for Cr(VI) reduction in the soil was 30 min. However, the reduction of Cr(VI) in soil may depend on the solubility and availability of aqueous Cr(VI), which is governed by the solid phase speciation reactions between labile Cr present on exchange sites and aqueous Cr. These equilibrium reactions will also be controlled by soil pH, composition of soil and soil pore-water.

7.3.1.3 Effect on Exchangeable Cr

The effect of Fe(II) on exchangeable Cr was similar to that recorded for soluble Cr (ie. Cr in the aqueous phase). In general, increasing levels of Fe(II) increased the reduction of phosphate exchangeable Cr in the contaminated surface soil (Fig. 7.3). A significant reduction was observed in the 0.5% (85%) and 10% (100%) $FeSO_4$ treated soils compared to the control. However, the decrease was more pronounced in soils with equilibration times exceeding 5h. The reduction in exchangeable Cr suggests enhanced transformation of Cr(VI) to Cr(III) in the presence of Fe(II). Comparing different reducing agents for potential remediation of chromate contaminated soils, James (1994) reported that Fe(II) was more efficient and completely reduced water-soluble and exchangeable Cr(VI) within 24 h after treatment. This suggests that in order to achieve complete reduction of Cr(VI) it may be necessary to equilibrate soils with $FeSO_4$ for a minimum of 24 h. Along with redox couples involving Fe(II), reduction of Cr(VI) in

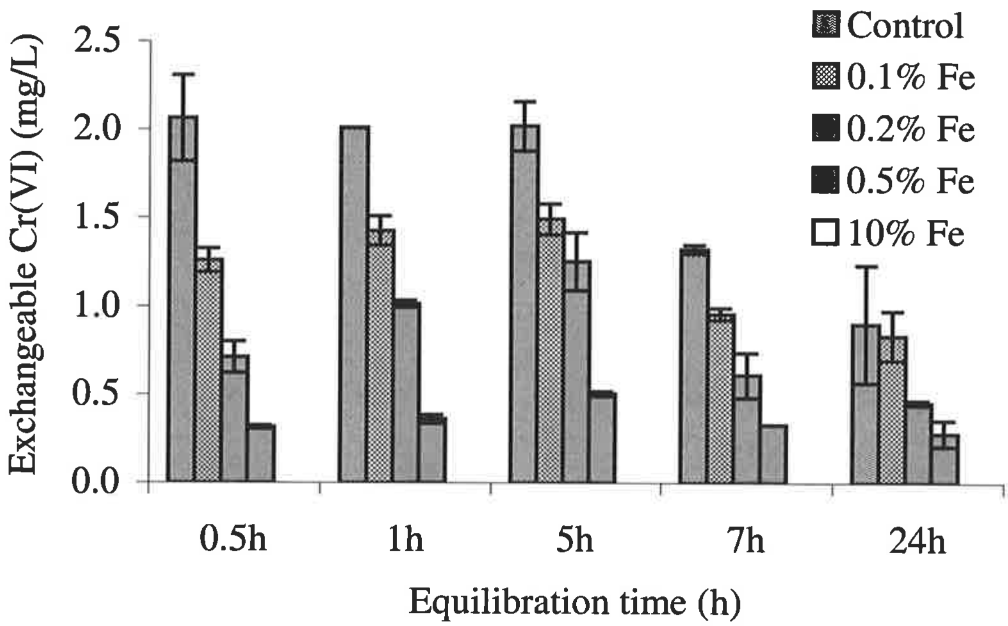


Fig. 7.3 Effect of Fe(II) on exchangeable Cr(VI)

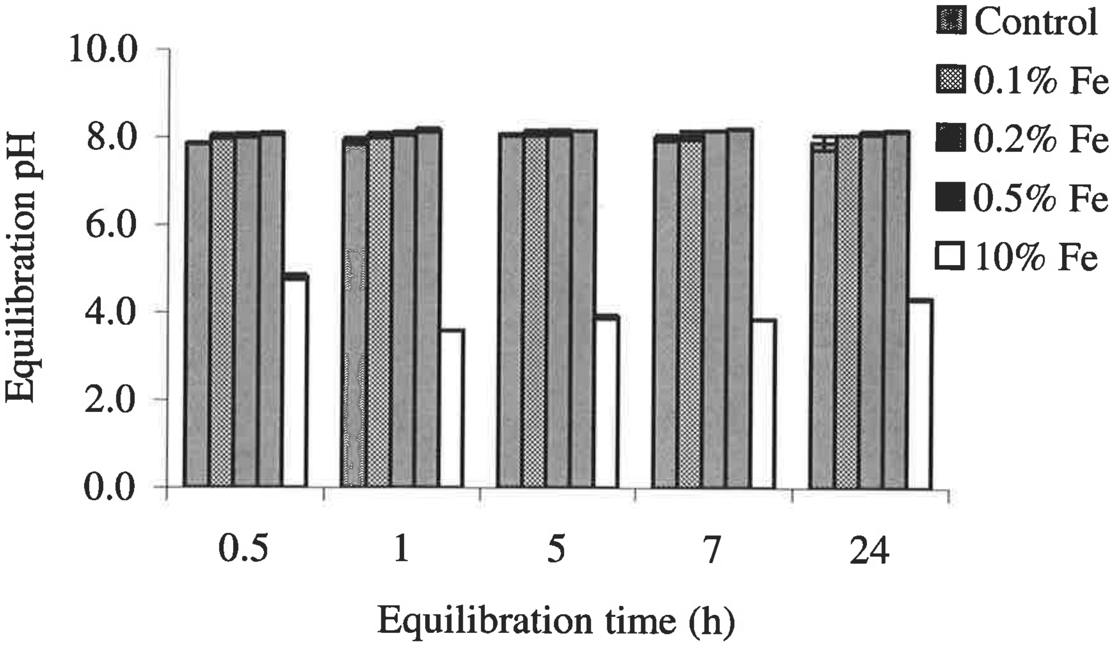


Fig. 7.4 Effect of Fe(II) addition on soil pH

soils is controlled by other factors such as pH, organic matter, Mn(II) and redox conditions. In the present study, transformation of Cr(VI) to Cr(III) is presumably only influenced by Fe(II) content and soil pH since all other factors were constant for all treatments. As shown in Fig. 7.4 increasing Fe(II) loading led to a significant decrease in soil pH, especially at the highest treatment, which also showed the maximum change in the nature of exchangeable Cr(VI).

Eary and Rai (1989) demonstrated that even small amounts of Fe(II) contained in hematite and biotite could reduce aqueous Cr(VI) species to Cr(III) resulting in the precipitation of $(Fe,Cr)(OH)_3$atm. These results suggest that soil conditions that enhance release of Fe(II) from silicate (Eq 7.2) or oxidic minerals may enhance the reduction of Cr(III). Thus the release of Fe(II) from silicate minerals in acidic solutions (Eary and Rai, 1989) or the reductive dissolution of Fe(III) silicates or oxides by organic acids (Hering and Stumm, 1990) can introduce Fe(II) to the soil solution.

$$[FeO]_{min} + 2H^+ \Leftrightarrow Fe^{2+} + H_2O \qquad \text{(Eq 7.2)}$$

In solutions with pH < 10.0, Fe(II) rapidly oxidises (Eq 7.3) and the nature of hydrolysis species depends on the pH of the solution (Eary and Rai, 1988).

$$3Fe^{2+} + HCrO_4^- + 3\,H_2O \Leftrightarrow CrOH_2^+ + 3Fe(OH)_2^+ \qquad \text{(Eq 7.3)}$$

7.3.1.4 Fe(II) for Optimum Reduction of Cr(VI) in the Contaminated Soil

It is apparent from the above study and that reported by James (1994) that a minimum 24 h treatment time is required for the optimum effect of Fe(II) on Cr(VI) transformation. The objective of the following studies was to optimize the Fe(II) loading to achieve complete reduction of Cr(VI). As discussed in the methods section varying concentrations of Fe(II) (1% to 7.5%) were added to contaminated soils and allowed to react over a 24 h period. The results from these studies revealed 90 – 100% reduction in water soluble (Fig. 7.5) and exchangeable Cr(VI) (Fig. 7.6) with an increase in Fe(II) loading from 1 to 7.5 % $FeSO_4$ (on soil weight basis) compared to the control surface contaminated soil, (without the addition of Fe(II)).

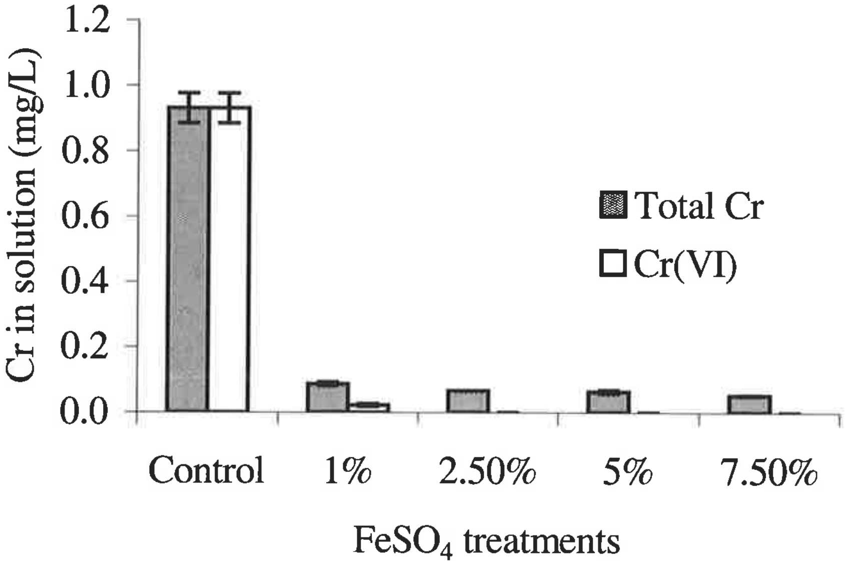


Fig. 7.5 Effect of Fe(II) on reduction of water soluble Cr

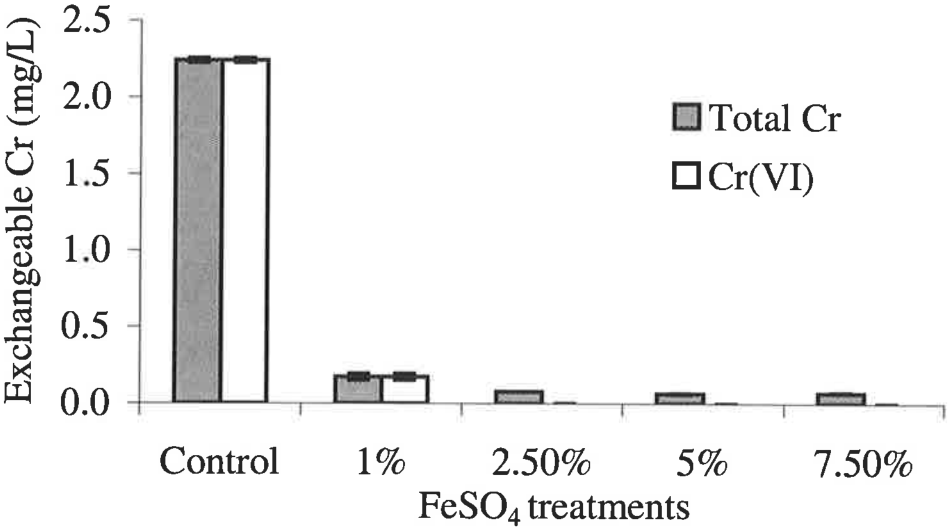


Fig. 7.6 Exchangeable Cr(VI) reduction by Fe(II)

7.3.1.5 Dynamics of Exchangeable Cr(VI) in the Presence of Fe(II)

The observed reduction of exchangeable Cr(VI) in the presence of Fe(II) suggests the presence of a highly labile pool of bioavailable Cr. Since soluble Cr(VI) is in equilibrium with labile Cr(VI) complete reduction of Cr(VI) is not surprising although the rapid kinetics of the Cr(VI) to Cr(III) transformation makes one question, the strength of binding between Cr(VI) and colloid surfaces. Based on Le Chatellier's principle of chemical equilibrium it is likely that the reduction of pore water Cr(VI) to Cr(III) leads to a rapid release of Cr(VI) from colloid surfaces into pore water to maintain the stability of the controlling Cr(VI)-colloid ⇔ Cr(VI) pore water equilibrium. James (1994) reported a similar reduction of exchangeable Cr(VI) by Fe(II) in chromite ore processing contaminated soils.

The relationship between increasing dose of Fe(II) and reduction of water-soluble and exchangeable Cr(VI) in this contaminated soil is presented in Fig 7.7. Under ideal conditions and in pure systems, 3 moles of Fe(II) are needed for complete reduction of 1 mole of Cr(VI) to Cr(III). The curvilinear relationship in Fig. 7.7 suggests loss of Fe(II) from soil pore water to reactions other than Cr(VI) reduction. In soils, loss of Fe(II) through sorption, complexation by organics and oxidation by atmospheric O_2 may limit oxidation of Fe(II) by Cr(VI). Thus more Fe(II) may be required for complete reduction of Cr(VI) in this highly contaminated soil. With an increase in Fe(II) loading beyond 2.5% a brown precipitate was observed indicating the formation of an Fe-(OH)x compound and possible loss of Fe(II) from pore water. Application of such high rates to contaminated soils therefore may not be economical. For this reason, the $FeSO_4$ application rate of 1 and 2.5% were used in the incubation experiments to evaluate the performance under field conditions where the moisture content was maintained at 50% field moisture capacity.

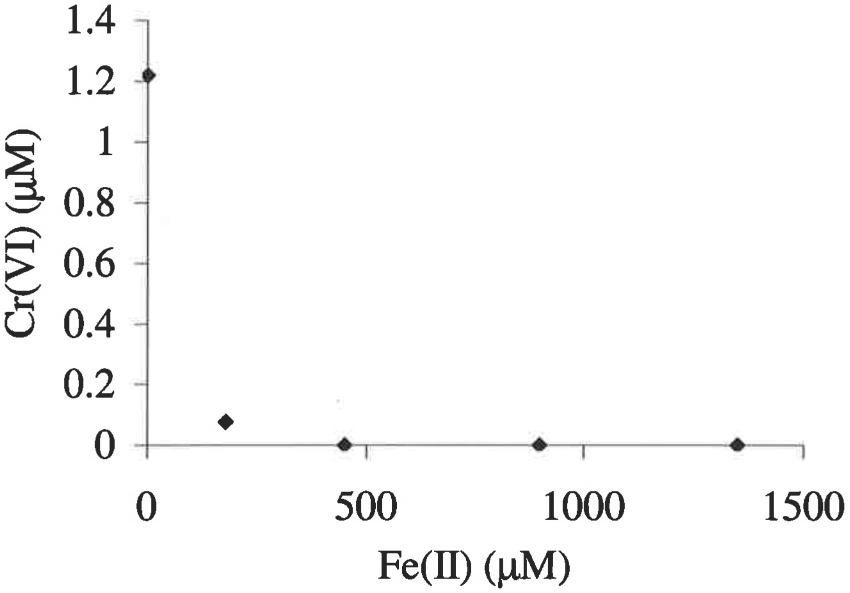


Fig. 7.7 The molar ratio of Cr(VI) reduction by Fe(II) in this contaminated soil

7.3.2 Incubation Studies

7.3.2.1 Effect of Increasing Fe(II) Loading on pH

A slight decrease in soil pH was observed in $FeSO_4$ treated soils compared to that of the control after 24 h of incubation. During 110 days of alternate wet, dry, wet cycles the pH only fluctuated within a narrow range (0.1 – 0.3 units) within the first 35 days and thereafter remained relatively constant (Fig. 7.8).

7.3.2.2 Soluble Cr in Pore Water

An appreciable decrease in the concentrations of soluble Cr was observed in the pore water collected after 3 h of incubation of soils with Fe(II) compared to the control. Over all, as expected, the effect of Fe(II) was more pronounced in the 2.5% $FeSO_4$ treated soil than in the 1% $FeSO_4$ treatments (Fig 7.9). The concentrations of soluble Cr released from the control soil were constant up to 85 days of incubation but showed a slight decrease in the pore water sampled after 110 days. In contrast to the control soil, water-soluble Cr in $FeSO_4$ treated soils increased with increasing duration of incubation up to 30 days. Beyond this period there was no significant change in pore water Cr concentrations (Fig. 7.9). The dry cycle did not have any significant effect on soluble Cr concentrations.

7.3.2.3 Reduction of Cr(VI) by Fe(II)

Complete reduction of Cr(VI) was observed in 3 h following incubation with $FeSO_4$ compared to control samples (Fig. 7.9). However, Cr(VI) reappeared in pore water in both 1% and 2.5% Fe(II) treated soils at day 2 and day 14, respectively. This was surprising

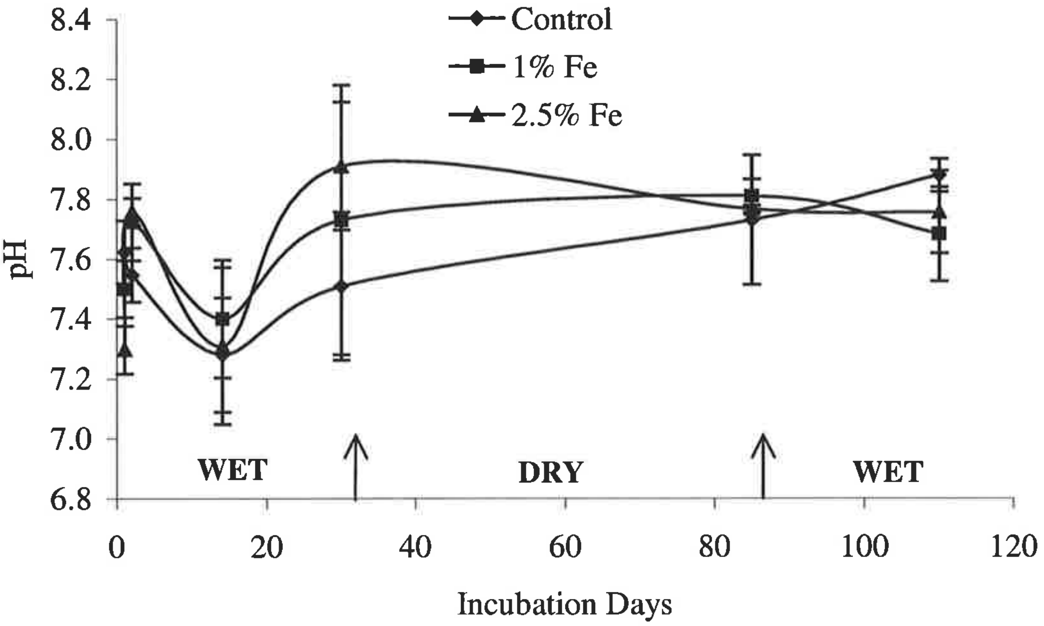


Fig. 7.8 Effect of $FeSO_4$ addition on soil pH during wet, dry and wet cycles

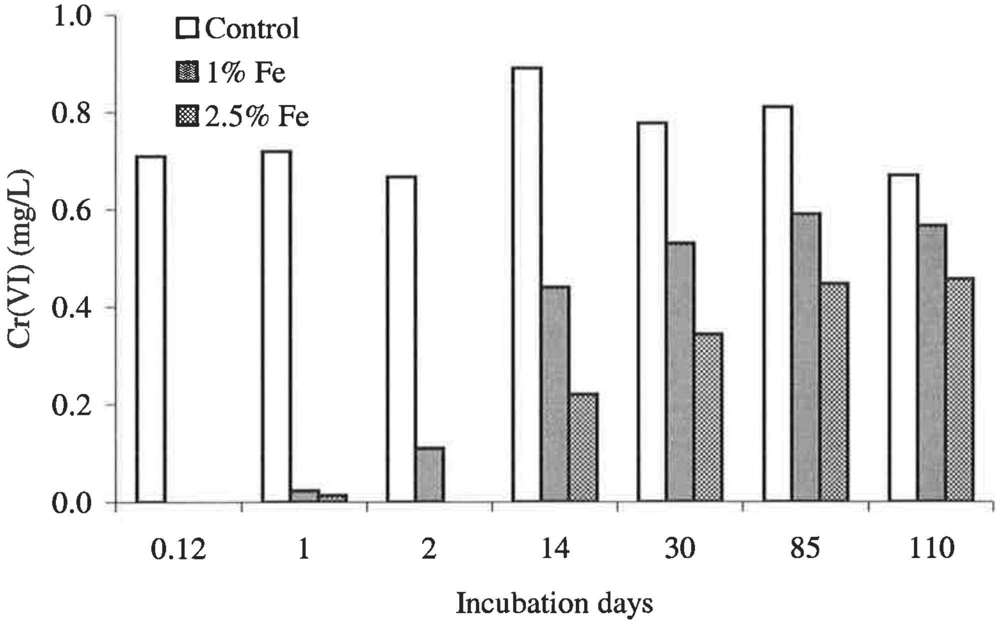


Fig. 7.9 Effect of Fe(II) on reduction of Cr(VI) during wet-dry-wet cycle

given that theoretical calculations suggest an excess of added Fe(II) in both treated soils. In the 2.5% $FeSO_4$ treated soil, the pore water concentration of Cr(VI) increased from day 14 and stabilized at day 85. Pore water concentrations of Cr(VI) in the control soils were constant (0.7 to 0.9 mg/l) up to 110 days of incubation beyond which there was a significant decline in Cr(VI) presumably indicating generation of redox conditions. The markedly different effect of varying Fe(II) loading on Cr(VI) reduction suggests that Fe(II) is the limiting reagent during the Cr(VI) reduction process. Clearly, the system has an excess of Cr(VI) despite the addition of 1% Fe(II). At the higher Fe(II) loading the amount of Cr(VI) reduced is greater, as Fe(II) persists for a longer period in the system as evidenced by the delay in the re-appearance of Cr(VI), day 2 for 1% loading compared to day 14 for 2.5% Fe(II) loading. Given that Fe(II) loading in these soils exceeds the minimum concentration needed for complete reduction of labile Cr(VI) the reappearance of Cr(VI) may also suggest loss of Fe(II) either via an ion exchange process or via oxidation of Fe(II) to Fe(III)(OH) which is an insoluble compound. Another possibility for the reappearance of Cr(VI) could be the oxidation of reduced Cr(III) by MnO_2 that may be present in the contaminated soil. The results for water-soluble Cr(III) indicate the presence of soluble Cr(III) up to 2 days of incubation irrespective of the $FeSO_4$ treatments (Fig 7.10).

Mn oxides are the only known naturally occurring oxidants of Cr(III) at $pH < 9$ (Eary and Rai,1987) that can readily oxidise this species (Fendorf and Zasoski, 1992). Although MnO_2 can readily oxidize Cr(III) the presence of Cr(III) at $pH > 7$ was surprising because at $pH > 5$ Cr(III) precipitates as $Cr(OH)_3$ (Eary and Rai, 1987). It is likely that the 50% field moisture incubated soils might have triggered microbially mediated reduction of Cr(VI) to Cr(III) (Llovera et al., 1993). However, low concentrations of Cr(III)

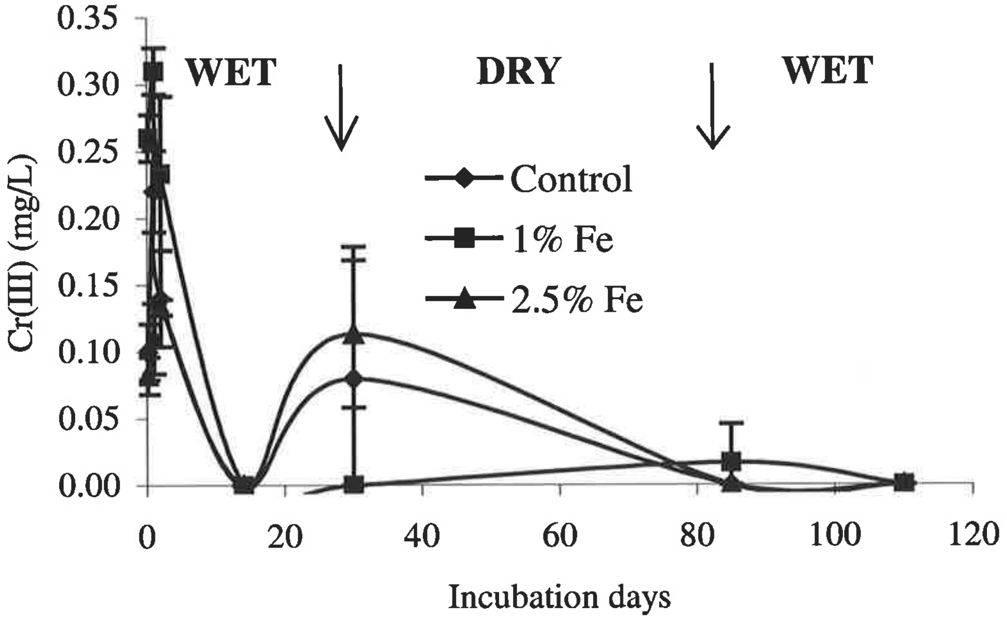


Fig. 7.10 Water soluble Cr(III) in Fe(II) treated soil during incubation

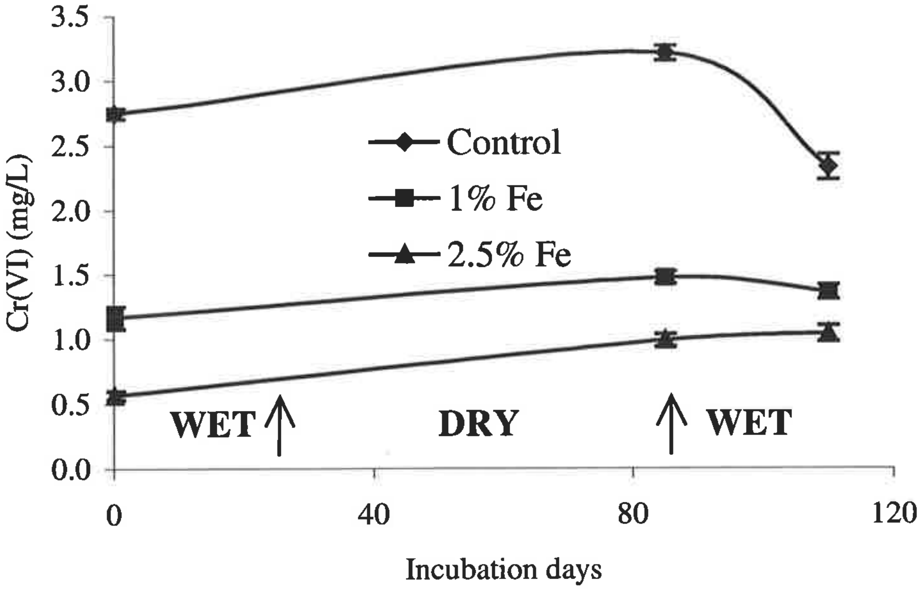


Figure 7.11 Reduction of exchangeable Cr(VI) by Fe(II) during wet-dry-wet cycle

were found in the pore water samples compared to the concentrations of Cr(VI) that reappeared from 14 day. In our laboratory studies, redox potential in freshly spiked Cr(III) and Cr(VI) soils was studied and the results showed that surface soil has low oxidation potential for spiked Cr(III) (0.2 – 0.3%) and high reduction potential for spiked Cr(VI) (85%) (Sara Kamaludeen, Personal communication). Hence, considering both the possibilities, it is likely that aqueous Fe(II) was limiting and this could be the reason for the reappearance of Cr(VI) despite addition of excess Fe(II) in the contaminated soil. The availability of aqueous Fe(II) after 24 h in 1% $FeSO_4$ and after 2 days in 2.5% $FeSO_4$ could also be limiting due to the oxidation of Fe(II) by atmospheric O_2, formation of Fe organic complex and sorption of Fe(II) to soil mineral surfaces.

7.3.2.4 Reduction of Exchangeable Cr(VI)

Similar to the observations recorded in the preliminary batch study, incubation of soils with $FeSO_4$ led to a marked decrease in the concentrations of exchangeable Cr(VI). The greater the amount of Fe(II) the greater the reduction of exchangeable Cr(VI) (Fig. 7.11). However, there was a significant (30 - 40%) increase in Cr(VI) following each dry period. The reduction of soluble and exchangeable Cr(VI) was significant during the initial wet period as long as soluble Fe(II) was present to reduce Cr(VI) to Cr(III). Once aqueous Fe(II) was depleted an increase in concentrations of water soluble Cr(VI) started to show from 14 days of the wet period and this process continued till the dry period. The increase in exchangeable Cr(IV) following the dry period of 85 days was significant. However, the reason for this increase was not clear. This increase was more pronounced in control samples compared to $FeSO_4$ treated soils and contrasted with wet periods, which after 25 days of incubation led to a marked decrease in Cr(VI) at the 110 day sampling for all the treatments. The reappearance of exchangeable Cr(VI) (Fig. 7.11) is consistent with the results observed for water soluble Cr(VI) (Fig. 7.9).

The water-soluble concentrations of Cr(III) were lower and also decreased with increasing $FeSO_4$ treatment. The most striking feature of this observation being the fact that Cr(VI) reappearance was linked to the amount of Fe(II) added. Increasing levels of Fe(II) led to a significant delay in the reappearance of Cr(VI). As discussed above (Section 7.3.2.3), one reason for the reappearance could be the large pool of labile Cr(VI) and the limitation on the amount of added Fe(II). This limitation in Fe(II) may be due to the loss of Fe(II) during ion exchange processes, oxidation to Fe(III)(OH), etc. In this contaminated soil Cr(VI) release may also be controlled by sparingly soluble compounds containing Cr(VI), such as $BaCrO_4$ (K_{sp} 1.2 X 10^{-10}) or $CaCrO_4$ (K_{sp} 7.1 X 10^{-4}) (James, 1994). The presence of $CaCrO_4$ would be consistent with the scanning electron microscopic studies reported by Thangavel and Naidu (2000) who provided evidence of Cr association with calcareous material. Based on Le Chatelliers Principle of chemical equilibrium, loss of Cr(VI) from soil pore water in the presence of Fe(II) would lead to release of Cr(VI) from the sparingly soluble salts and exchange sites to maintain the thermodynamic stability constant, especially when Fe(II) becomes the limiting reagent.

7.3.2.5 Exchangeable Cr(III)

Appreciable concentrations of exchangeable Cr(III) were observed in control soils compared to $FeSO_4$ treated soils (Fig. 7.12). However, exchangeable Cr(III) was greater than that recorded during batch Cr(VI) reduction experiments. The prolonged incubation period would favor both abiotic and direct enzymatic reduction of chromate by microorganisms and also favor the reduction of Cr(VI) by the high organic matter content of the contaminated soil (Ishibashi et al., 1990; Bartlett and Kimble, 1976b). Both biotic and abiotic reduction of Cr(VI) in these soils are to some extent supported by the high organic matter content (Chapter 4) and the Cr(III) formed in the presence of organic matter could be associated with soluble chelated complexes with organic reductants (James and Bartlett, 1983c). Sorption of Cr(III) to freshly precipitated Fe oxy hydroxides in $FeSO_4$ treated soils could also lead to an appreciable decrease in Cr(III) concentration. In Section 7.3.1.3 factors controlling Cr(VI) reduction to Cr(III) have been discussed in considerable detail.

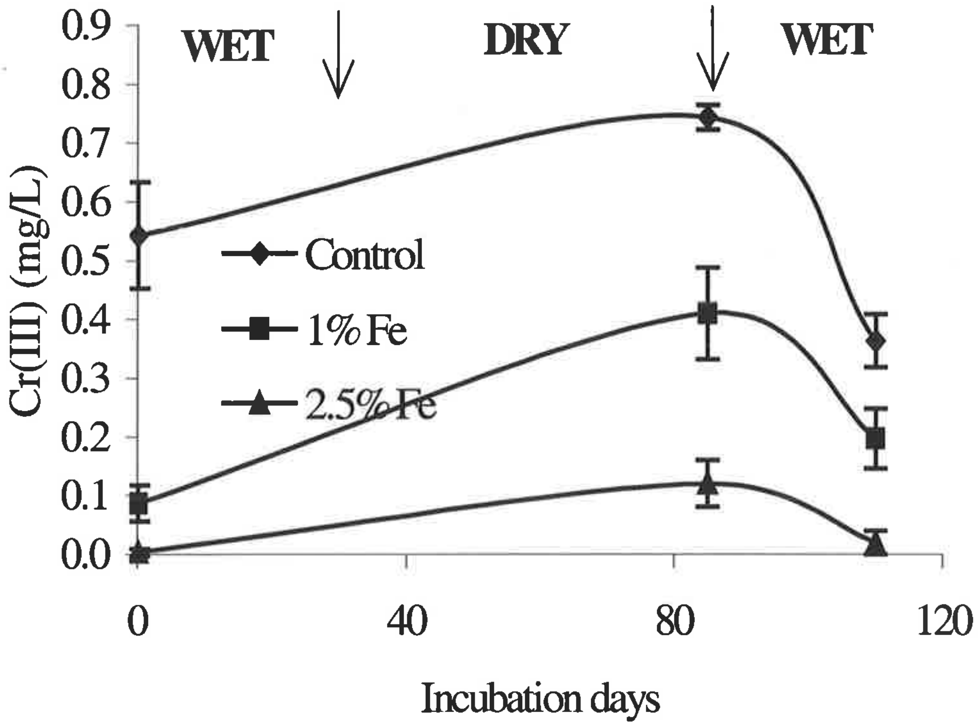


Fig. 7.12 Concentrations of exchangeable Cr(III) in Fe(II) incubated conditions

7.4 Conclusions

The following conclusions were drawn from the present study:

- Iron sulphate proved to be an effective agent for the reduction of water-soluble and exchangeable Cr(VI).
- Kinetics of Cr(VI) reduction by Fe(II) under batch conditions showed that the reduction reaction was rapid and that a low $FeSO_4$ dose (0.1 – 0.5 % on a soil weight basis) may not be enough to completely reduce the water-soluble and exchangeable Cr(VI) present in the soil.
- An increase in desorption of Cr(VI) with increased equilibration time was observed.
- A large excess molar ratio of Fe(II) (1 – 2.5% of $FeSO_4$ on soil weight basis) completely reduced the water-soluble and exchangeable Cr(VI) of this soil under batch conditions. Soil pH was decreased from 7.66 to 6.93 but no visual brown precipitate of amorphous Fe oxide was observed as a consequence of 1 – 2.5% $FeSO_4$ applications.
- The optimal dose of Fe(II) (1 – 2.5% $FeSO_4$) calculated from batch conditions did not completely reduce the water-soluble and exchangeable Cr(VI) under a soil moisture content fixed at 50 % field capacity. Reappearance of Cr(VI) was observed after showing an initial reduction of water-soluble and exchangeable Cr(VI) in the $FeSO_4$ incubated soils. The dry cycle significantly increased the concentrations of exchangeable Cr(VI) in this contaminated soil. The rate of desorption of Cr(VI) or solubility of Cr(VI) in this contaminated soil could be a limiting factor for complete reduction of water-soluble Cr(VI) by Fe(II).

CHAPTER 8

In-situ Stabilization of Chromate in Tannery Waste Contaminated Soils: Intact Core Studies

8.0 Introduction

It is evident from the laboratory incubation studies conducted under controlled conditions (described in Chapter 7) that iron sulfate ($FeSO_4$) could be an effective reductant of Cr(VI) present in the contaminated soils. While the laboratory studies are critical in assessing the potential of various remedial options, the effectiveness of remediation options under field conditions cannot be established from such studies. Bench scale assessment of remediation technology is the obvious next step. Therefore, the outcomes of the laboratory incubation studies were used to investigate the potential for remediating Cr(VI) in the contaminated soil using intact cores collected from the contaminated site. The specific objective of the study described in this chapter is to assess the effectiveness of surface mixed $FeSO_4$ in reducing and stabilizing the chromate present in both surface and subsurface layers at the contaminated site. In this chapter, the leaching behavior of Cr through an intact core following treatment of the surface soil layer with $FeSO_4$ is discussed with a view to establishing the potential effectiveness of such a treatment for transforming Cr(VI) to Cr(III) and thus rendering it immobile.

8.1 Materials and Methods

8.1.1 Site and Soil

The study was conducted on ~~the~~ an intact core collected from the site contaminated with tannery waste located at Mount Barker, South Australia (see Chapter 3 for more details). This site was used for tannery effluent and waste disposal until the early 1980's. The total Cr concentrations at the site ranged from 0.1 to 62 g/kg in the top 30 cm of the soil profile. The Cr concentration gradually decreases below this depth to 0.26 g/kg (Table 3.1 in Chapter 3). Nevertheless the Cr concentrations of the subsurface soils at this site often exceeded 1000 mg/kg. The soil at this site is duplex soil, that is it posses a sandy surface and clayey subsurface horizons (Naidu et al., 2000a). The heavy contamination of the soil profile with Cr(VI), together with elevated pH, makes the potential for leaching of Cr (VI) high. Indeed, as observed from batch studies (Chapter 5, Section 5.3.2) and repacked column experiments (Chapter 6, Section 6.3.1), the water soluble Cr(VI) concentration leached from surface soil was significantly higher than the threshold limit of 0.05 mg/L for groundwater. The intact core soil was collected from the hot spot at the contaminated site and was from the same spot where the soil profile was dug to collect soil samples for other experiments reported in the earlier chapters.

8.1.2 Preparation of Intact Cores

Manually pushing a PVC pipe through the soil and carefully tapping the top of the pipe with a wooden hammer collected the intact core (10 cm in diameter and 30 cm in length). Once the entire PVC length was driven through the profile, soil around the pipe was removed and the core carefully excavated. The two ends of the column were capped and transported to the laboratory. The intact core was prepared for the transport study by removing a few centimeters of soil from the bottom of the core in order to obtain a reasonably smooth surface while leaving a 2 - 3 cm collar of empty column. This space was filled with a layer of acid-washed sand to facilitate the flow into the funnel leading to the collection vessel. A nylon cloth was glued to the bottom of the column to hold the sand in place. The bottom of the column was capped and a small opening in the middle of the cap was fitted with a funnel for leachate collection. To facilitate the sampling of pore waters from two depths in the soil columns, sampling ports were provided (see Plate 8.1)

The leaching solution (distilled water) was fed through a custom-designed delivery head fitted with hypodermic syringes and needles to cover the entire cross-sectional area of the column. The flow through the needles was controlled using a peristaltic pump connected to an airtight reservoir on top of the nest of needles. The leaching solution was thereafter introduced to the soil surface in a form simulating raindrops (Plate 8.1).

8.1.3 Application of Fe(II) Salt and Equilibration

On the basis of the results obtained from studies described in the previous chapter, the quantity of Fe(II) salt applied was increased to 3% on a soil weight basis for the intact core study. A higher dose of the Fe(II) salt was used to achieve complete reduction of Cr(VI) in the surface soil and also for reduction of Cr(VI) present in the subsurface soil due to migration. Lower amounts of Fe(II) had not been sufficient for the complete reduction of water-soluble and exchangeable Cr(VI) in the incubation studies (see Chapter 7, Sections 7.3.2). Iron salt (3% $FeSO_4$, 6.24 g) was added to the surface of the soil up to a depth of 5 cm by calculating the weight of soil to this depth.

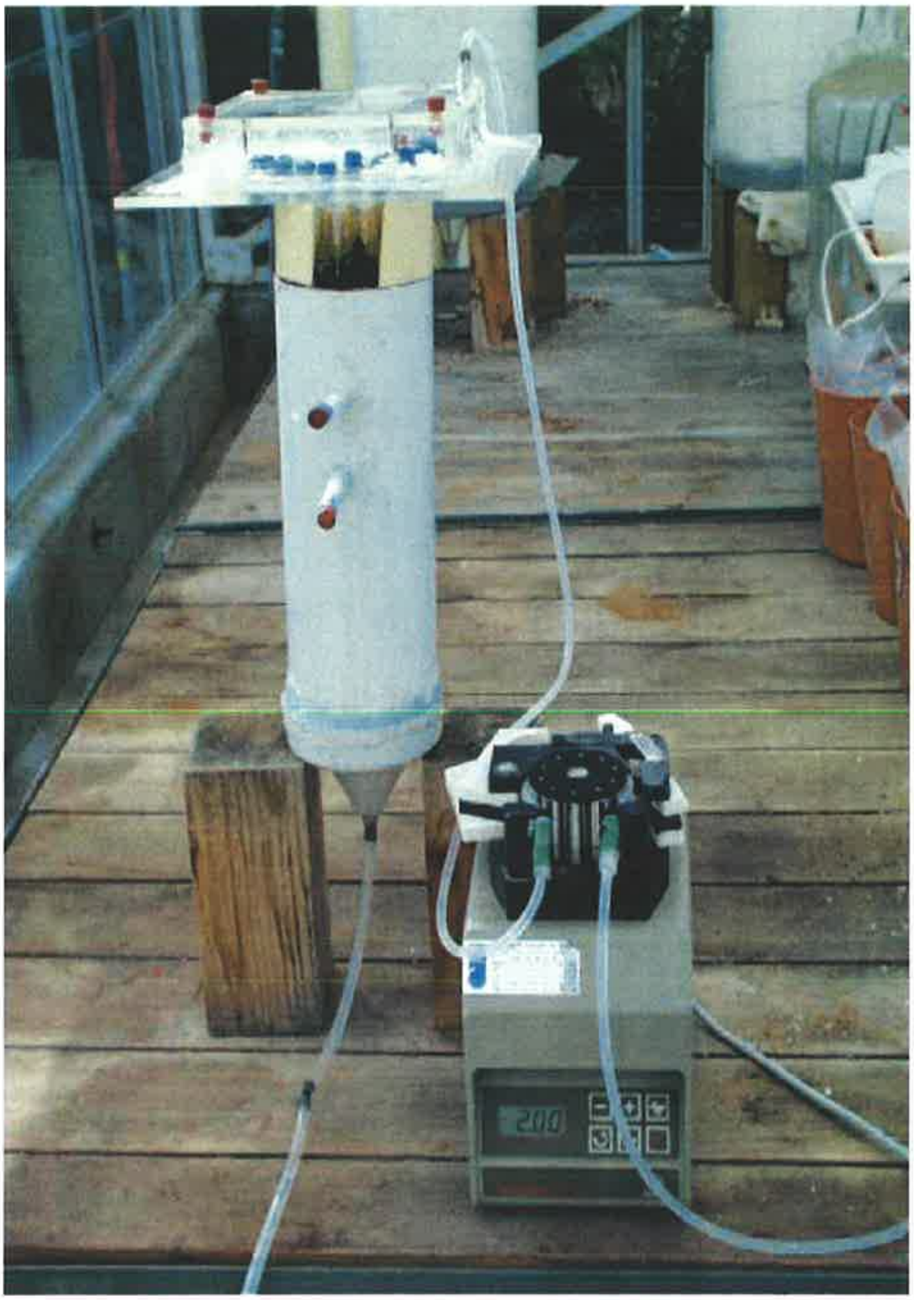


Plate 8.1 The set-up for the column leaching experiment.

The Fe(II) salt was thoroughly mixed to a depth of 4.5 cm without disturbing the sample port set at a depth of 5 cm. After mixing the surface was made even and to avoid preferential flow along the walls of the core Vaseline™ petroleum jelly was placed around the core wall. The Fe(II) was allowed to equilibrate with the soil for at least 24 h before introducing the leaching solution.

8.1.4 Fiberglass Wicks as Sampling Ports

The main objective of *in-situ* stabilization experiments was to assess the effectiveness of surface applied Fe(II) to reduce Cr(VI) present in both the surface and subsurface layers of the site. Therefore sampling ports were installed to collect samples immediately after the Fe(II) treated layer and the layers thereafter. Fiberglass wicks quenched with phosphate had previously been shown to be inert for Cr(VI) and effective as sampling ports (Kookana, et al., 2000) and hence the same technique was used in the present study. The 6 cm long phosphate-quenched wicks were washed twice with water and inserted in to 5 cm long plastic tubes, such that about a cm of wick protruded outside the tube enabling pore water to be sampled by suction. Holes of about the diameter of the tube were drilled 4 cm into the column at 5 cm and 10 cm depths. The tube section to be embedded in soil was split in such a way that the top of the wick was in intimate contact with soil but the lower half of the wick was only in contact with the plastic lip thereby preventing contact with the soil solution below that point. The tubes fitted with wicks were inserted into the holes up to 3.5 cm and sealed with silicone. Samples were obtained by applying a small amount of suction with the help of hand-held hypodermic syringes and needles inserted through the wicks.

8.1.5 Flow Rate and Sample Collection

The soil column experiment was conducted in a glasshouse maintained at 20 ± 2 °C. Initially the column was saturated with distilled water at a high flow rate of 10.6 mL/min and once leachate was observed at the bottom the flow rate was decreased to 1.0 mL/min and continued until the end of the run. At regular intervals leachate samples were collected from the bottom and from the 5 and 10 cm sample ports. The volume of leachate collected at the bottom was recorded at the time of each sample collection. Sub-samples of the leachate were passed through 0.45 μm syringe filters and stored in polystyrene containers for further analysis. The pH, total Cr , Cr(VI), total S, and total Fe were measured using the analytical methods described below. Chromium speciation was conducted immediately after leachate collection to prevent reduction of Cr(VI) during storage.

8.1.6 Non-reactive Tracer Study

A 50 mg/L Br^- solution was leached through the column at the same flow rate (1.0 ml/min) after 4.4 pore volumes (PV) to characterise the flow through the column. The Br^- leaching was continued until a complete frontal breakthrough curve (BTC) was obtained. Following this distilled water was leached through the column. The Br^- concentration in sub-samples from the leachate was analysed by ion chromotagraphy. During the Br^{-1} leaching, samples from ports were not collected. However, total Cr and Cr(VI) concentrations were measured for the sub-samples collected from leachate exiting the column.

8.1.7 Methods of Analysis

The pH was measured using an ORION pH meter, total Cr in the solution was determined using FAAS or GFAAS, Cr(VI) by ion chromatography and the difference between total Cr and Cr(VI) was considered to be Cr(III) in solution. Total Cr in solution was measured by flame atomic absorption spectrometry using the method described in APHA, 1992. Solution Cr(VI) was measured by Ion chromatography (DIONEX, Model 4000I, California, USA) using the Method 7199 developed by U.S.EPA (USEPA, 1996) for the determination of Cr(VI) in drinking water, ground water and industrial wastewater effluents. The detailed procedures were described in Chapter 3, Section 3.2. Cations and anions in solutions were analyzed using inductively coupled plasma emission spectroscopy (ICP-AES, spectro flame modula, spectroanalytical instruments GMBH, Germany).

8.2 Results and Discussion

8.2.1 Column Charactrestics from the Tracer Study

The breakthrough curve of the non-reactive tracer Br^- showed a near symmetrical curve, typically representing matrix flow rather than preferential flow, which may occur along column walls. From the breakthrough curve it was inferred that the column showed no biomodal distribution, no preferential flow paths and sealing through Vaseline was effective (Fig. 8.1). The breakthrough data was used to calculate the pore volume according to the method given by (Rose, 1977). One pore volume was found to be 1700 mL at 0.5 of C/C_0, representing a porosity value of 0.7 cm^3/cm^3. The high organic content of the soil (10 %) may have resulted in such a high value. However, it shows that little bypass flow occurred during the leaching of solution.

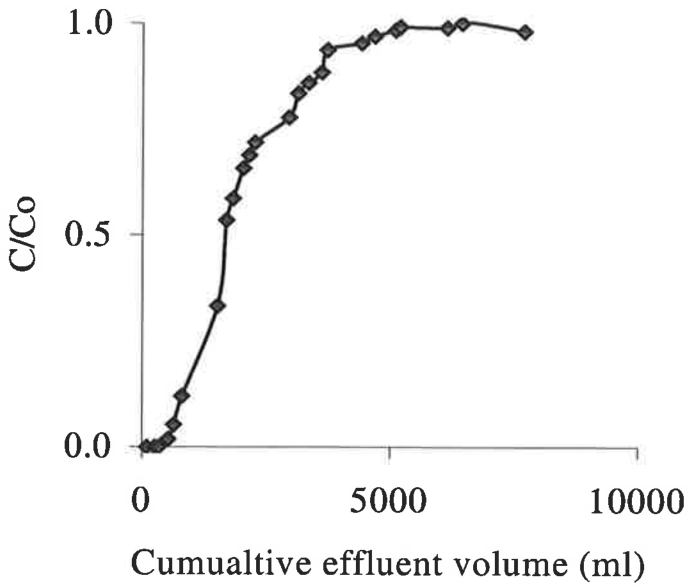


Fig. 8.1 Breakthrough curve of the non-reactive tracer Br$^-$

8.2.2 Pore Water Chemistry of the Treated Zone (5 cm)

The ~~leachate~~ pore water collected from the Fe(II) treated zone through the port located at 5 cm depth showed a total Cr concentration of 60 to 90 μg /L on day one, which gradually decreased to 30 μg/L by day six of leaching. The concentration of Cr released was 0.2% on day one and decreased to <0.1% on day six out of the total Cr(VI) (40 mg/kg) present in the surface soil. Following this period, on day seven, the Cr concentration increased to 60 μg/L and continued to increase up to day 10 of leaching when a concentration of 80 μg/L was recorded. Surprisingly, the speciation of Cr showed soluble Cr(VI) and soluble Cr(III) in equal proportion up to day six. However, from day seven Cr(VI) was the dominant species found in the ~~leachate~~ pore water collected from the 5 cm sample port (Fig. 8.2).

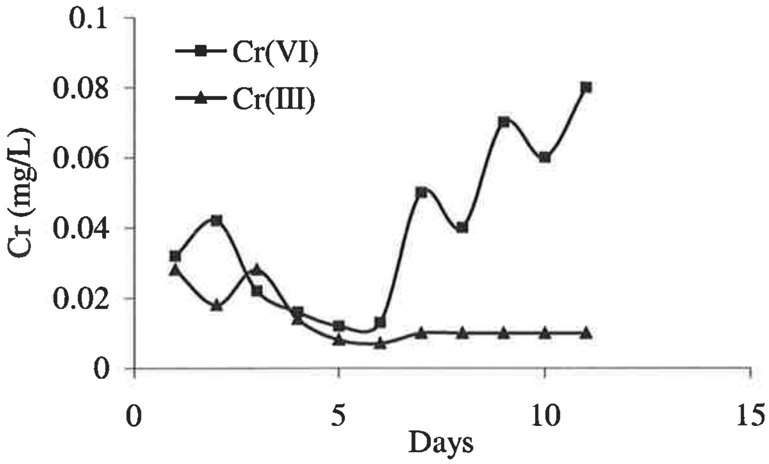


Fig. 8.2 Concentration and speciation of Cr in leachate from the 5 cm sample port

It appears that the $FeSO_4$ treatment partially reduced the pore water Cr(VI). Therefore the pore water from the treated zone showed initially low Cr(VI) concentrations. As leaching progressed, fresh Cr(VI) was released from the aggregates and was not reduced due to lack of available Fe(II). The increased Cr(VI) with time probably indicates gradual oxidation of Fe(II) to Fe(III) during Cr(VI) reduction. Obviously the soil contained a very large reservoir of Cr(VI) (The concentration of single phosphate extractable Cr(VI) was 10 mg/kg).

The pore water ~~leachate~~ collected from the 5 cm sample port showed a large concentration of Ca in the range 700 to 780 mg/L on day one which decreased gradually from day two. On day 7 Ca concentration had decreased to 102 mg/L. Apart from Ca, the pore water ~~leachate~~ from the 5 cm depth also contained high concentrations of Mg and Na. The Mg concentration varied between 25 to 30 mg/L on day one and gradually decreased to 3 mg/L on day 7. Similarly Na concentration decreased from 30 to 45 mg/L on day one to 4 mg/L on day 7. No detectable Fe concentration was found in the pore water ~~leachate~~ collected from the 5 cm sample port indicating complete removal of Fe(II) from the soil pore water. This may be one reason for the continued presence of Cr(VI) in the soil leachate. A low concentration of Mn was found on day one and two, 0.67 and 0.55 mg/L respectively and no detectable Mn was observed in the leachate from day three onwards. The leachate from the 5 cm port contained a high concentration of ~~sulfur~~ sulphate-S on day one (525 to 725 mg/L) that decreased gradually from day two. The pH of leachates collected from Fe(II) treated zone was increased from 8.1 to 8.3. The concentrations reflected the high salt content of the profile originating from the tannery waste (Table 8.1).

Table 8.1 Concentration of cations, anion and pH of the effluent from the Fe(II) treated zone (5 cm)

Days after Treatment	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	S (mg/L)	Mn (mg/L)
1	8.1	768.1	31.1	45.1	575	0.67
2	8.1	509.0	10.5	33.2	405	0.55
3	8.2	283.3	12.0	15.3	194.2	0.0
4	8.2	174.2	6.1	8.8	109.0	0.0
5	8.3	144.0	4.8	8.3	80.2	0.0
6	8.2	125.4	4.1	6.2	68.2	0.0
7	8.3	102.0	3.2	4.4	52.3	0.0

8.2.3 Chromium and Pore Water Chemistry of the Layer Immediately Below the Fe(II) Treated Zone

Total Cr concentration in the leachate sampled from the 10 cm port was 20 times higher than the Cr concentration observed in leachate from the Fe(II) treated zone above the 5 cm port on day one. The Cr concentration gradually decreased from 0.7 mg/L on day one to 0.11 mg/L on day 11 (Fig. 8.3).

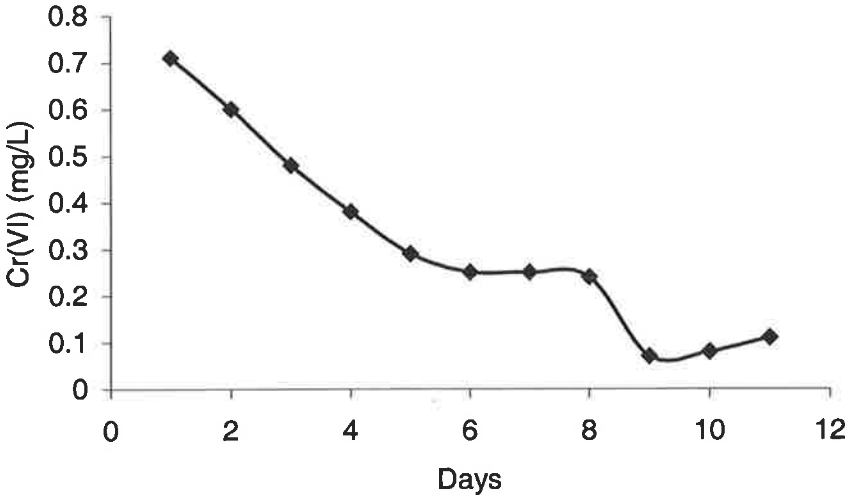


Fig. 8.3 Concentration of Cr(VI) in leachate from the 10 cm sampling port

Speciation of Cr in the the leachate collected from the 10 cm sampling port showed that all of the Cr leached from this zone was probably in the Cr(VI) form and no Cr(III) was detected in the leachate. Unlike the low concentration of Cr(VI) recorded in the pore water from the treated zone, the concentration at the 10 cm depth was high and did not increase with time.

The leachate from 10 cm showed high concentrations of Ca (447 mg/L) and S (296 mg/L) on day one, which gradually decreased, to 49 mg/L and 21 mg/L for Ca and S respectively on day 7. This trend was similar to that observed for leachate collected from 5 cm port except that the Ca, Na, Mg and S concentrations were lower than observed in the Fe(II) treated zone (Table 8.2). Na (53 mg/L) and Mg (16 mg/L) concentrations on day one were lower than the concentrations observed in leachate collected from the 5 cm port. Similar to the trend of gradual decrease in Ca and S concentrations, Na (3 mg/L) and Mg (0.14 mg/L) concentrations in the leachate decreased on day 7. The considerable release of soluble cations and sulphate from the intact core indicated that the contaminated site presumably received these salts from tanning industry waste. As observed in leachate from the 5 cm port, no soluble Fe was detected in the leachate from the 10 cm port. This indicated that all the incorporated Fe(II) salt was either oxidized by Cr(VI) or lost through soil adsorption or oxidation by O_2. The high soil pH also favours adsorption in preference to migration of Fe to subsurface layers. No definitive trend in Mn release was observed since only a single low concentration (0.2 mg/L) was detected on day two. The leachates from the 10 cm port recorded a slight pH increase from 8.2 to 8.5 through out the leaching period.

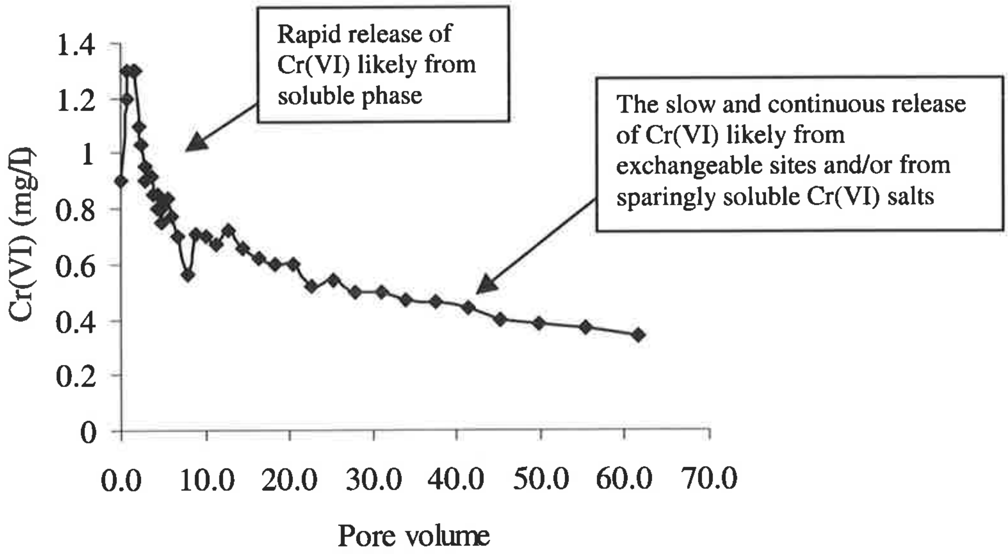
Table 8.2 Concentration of cations, sulfur and pH from the port immediately below the Fe(II) treated zone (10 cm)

Days after Treatment	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	S (mg/L)	Mn (mg/L)
2	8.2	447.3	15.6	53.1	346.1	0.0
3	8.2	168.0	3.0	16.0	104.0	0.2
4	8.2	100.0	1.1	10.4	43.5	0.0
5	8.4	77.0	1.0	10.0	30.4	0.0
6	8.3	56.4	0.3	3.7	11.6	0.0
7	8.5	49.1	0.1	3.1	10.3	0.0

8.2.4 Pore Water Chemistry of Effluent from the 10-30 cm Zone

The effluent collected from the 10-30 cm zone showed higher Cr concentrations than those detected in the 5 cm port leachate and was even greater than that detected in the leachate from the untreated zone at 10 cm. During the first four days, Cr concentration in the leachate ranged from 0.9 to 1.3 mg/L. However, Cr concentration gradually decreased in the leachate during subsequent days to 0.3 mg/L on day 16.

Speciation studies showed that Cr in the effluent was predominantly Cr(VI). This suggests that Fe(II) incorporated on surface layer was not effective in reducing soluble Cr(VI) in the 10 - 30 cm layer. Since the effluent volume ~~from~~ the exit point was measured during the experiment, the number of pore volumes could also be calculated. Even after 60 pore volumes the Cr(VI) concentration leached from the 30 cm exit zone was still above the permissible limit of Cr (VI) concentration (0.05 mg/L) for groundwater (Fig. 8.4). The Cr (VI) concentration dropped sharply within the first 10 pore volumes and subsequent leaching showed Cr was released at a much slower rate. This again indicated the continuous release of Cr (VI) out of aggregates and/or organic matter into the pore water. The continuous release of Cr(VI) is consistent with the observation made in leaching studies using the same contaminated surface soil in repacked glass columns (Chapter 6 (Fig. 6.6)).



Rapid release of Cr(VI) likely from soluble phase

The slow and continuous release of Cr(VI) likely from exchangeable sites and/or from sparingly soluble Cr(VI) salts

Fig. 8.4 Concentration and speciation of Cr in the effluent from exit zone (30 cm)

From the 10 - 30 cm layer nearly 2.5% of the concentration of Cr(VI) was released in the first pore volume out of a total possible 40 mg/kg of Cr(VI) present in the layer compared to < 0.1% Cr(VI) found in the leachate collected at 5 cm. The initial relatively rapid release of Cr from this zone is presumably due to the high soil pH and possibly due to the presence of sparingly soluble Cr salts accumulated in this zone. Indeed, SEM studies conducted using surface and subsurface soils from the contaminated site showed the presence of Cr on calcareous surfaces. The relatively sharp decrease in the amount of Cr removed during the course of extractions is probably a reflection of the decrease in the amount of sparingly soluble Cr salts. The slow continuous release after 10 pore volumes suggests that Cr(VI) may be released from a large reservoir of exchangeable Cr(VI) or from a sparingly soluble Cr(VI) pool. Straight line extrapolation using the linear least squares method ~~of~~ relating observed pore volumes and Cr(VI) concentration leached, predicted that it may take another 40 pore volumes to reach the threshold Cr(VI) concentration of 0.05 mg/L for drinking water. The continuous release of Cr(VI) from the contaminated soil profile may eventually contaminate the ground water aquifer of the site. Indeed, earlier studies in this laboratory showed the presence of Cr(VI) in ground water immediately below this contaminated site (Naidu et al., 2000a). Clearly, the $FeSO_4$ treatment in the top 5 cm zone of soil had no influence on the Cr concentrations leaching ~~from~~ below the 30 cm depth.

Ca, Na, Mg and S concentrations in the effluent from the exit point at 30 cm showed trends similar to that observed for leachate collected from 5 and 10 cm ports (Table 8.3). Initially salt release was high and gradually decreased with time. The concentration of Ca, Na, Mg and S on day one was 532, 51, 22 and 297 mg/L respectively. While on day 7 the concentrations of Ca, Na, Mg and S had gradually decreased to 77, 7, 2 and 21 mg/L respectively. As observed in the treated zone at 5 cm and the untreated zone at 10 cm effluent from exit zone at 30 showed no evidence for the presence of soluble Fe. Again, the release of Mn showed no definitive trend except for a single low concentration (0.2 mg/L) observed on day two. The pH of the effluent from exit point increased from 7.7 to 8.2 over seven days. The large concentration of salt in the column was responsible for the high salt loading in the effluent.

Table 8.3 Concentration of cations, sulfur and pH of the effluent from the 10 - 30 cm zone (column exit point)

Days after Treatment	pH	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	S (mg/L)	Mn (mg/L)
1	7.7	531.5	22.2	51.2	297.0	0.0
2	7.7	437.3	18.2	37.2	258.0	0.2
3	7.7	394.0	6.3	15.2	291.0	0.0
4	7.7	134.3	1.7	10.8	74.1	0.0
5	8.1	119.0	3.4	10.6	51.0	0.0
6	8.1	104.0	3.5	11.2	40.0	0.0
7	8.2	77.0	21	6.7	21	0.0

8.2.5 Effect of Fe(II) on Stabilization of Cr(VI) in the Treated Zone

The Cr concentration observed for pore waters and leachates from the 5, 10 and 30 cm ports indicated that Fe is critically needed for the reduction of Cr(VI) to Cr(III) and that surface applied Fe, while applied at concentrations that exceed the amount required for complete Cr(VI) reduction, was not sufficient for subsurface Cr(VI) reduction. The Cr concentration measured in pore water collected after 24 h of Fe(II) equilibration from the 5 cm port was 20 to 30 times lower than the Cr concentration observed at the 10 cm port and at the exit zone at 30 cm. This equates to nearly 95% reduction of the soluble

Cr(VI) in the Fe(II) treated zone compared to the untreated zone. Also the presence of soluble Cr(III) in the ~~leachates~~ pore water from the 5 cm port during the first three to four days indirectly indicate that the reduction of Cr(VI) to Cr(III) had taken place in the Fe(II) treated zone. Hydrolysis of Cr(III) at high soil pH would have gradually decreased Cr(III) availability in subsequent days.

Consistent with the observation of reduction of soluble Cr(VI) by Fe(II) in batch and incubation experiments, application of Fe(II) up to a depth of 4.5 cm in the intact core reduced soluble Cr(VI) to Cr(III). These results are similar to the observations of James (1994) and Seaman et al., (1999), who also observed the reduction of water soluble and exchangeable Cr(VI) using the ferrous iron. However, one major difference was observed here in soil pH compared to the Fe(II) treatments in batch and incubation studies. In batch studies a 10% Fe(II) application based on the soil weight decreased soil pH by 4 units (Fig. 7.4, in Chapter 7) and in incubation experiments a 2.5% Fe(II) application decreased soil pH by 0.6 units. However, no such decrease in soil pH was observed in the 3% Fe(II) treated zone for the intact soil core soil. In fact, Fe(II) treated and untreated zones exhibited an over all increase in soil pH from 7.7 to 8.5. The marked decrease in soil pH during incubation and batch studies is not surprising as in both instances a forced equlibrium is achieved in the closed system where there is no loss of salt. In contrast, intact core studies present an open system in which the leaching enhances removal of salt from the system, especially S as SO_4 and other major cations. During this process there was significant loss of hydrogen ions and also a decline in ionic strength of the interstitial water which must lead to increased pH in these negatively charge soil system. It is also likely that a 24 h contact time was not sufficient for chemical reactions to occur prior to leaching studies.

8.2.6 Reappearance of Cr(VI) in the Fe(II) Treated Zone

Although the Fe(II) treated zone showed significant reduction in soluble Cr(VI) within 24 h, after a gradual decrease in the concentration of Cr(VI) at day 7 Cr(VI) concentration started to increase (Fig. 8.2). These results are consistent with the reappearance of Cr(VI) as observed in batch and incubation studies.

As discussed in Chapter 7 (Section 7.3.2.3), one reason for the reappearance could be the large pool of labile Cr(VI) and the limiting amount of Fe(II) added. This limitation in Fe(II) may be due to (a) leaching of Fe(II) to subsurface soils (but no Fe(II) was detected in the leachates from subsurface ports), (b) the loss of Fe(II) during ion exchange processes and oxidation to Fe(III)(OH). Troug (1948) reported that as the pH increased above 6.5, soluble ferrous iron (Fe(II)) tend to become oxidised to ferric oxide Fe(III) which was insoluble under neutral and alkaline conditions. This may also be true the in Fe(II) treated zone. Oxidation of Fe(II) to Fe(III) had limited the migration of Fe to subsurface layer to effect reduction of Cr(VI) in the subsurface layers. Cr(VI) release in this contaminated soil may also be controlled by sparingly soluble compounds containing Cr(VI), such as $BaCrO_4$ (K_{sp} 1.2 X 10^{-10}) or $CaCrO_4$ (K_{sp} 7.1 X 10^{-4}) (James, 1994). The earlier incubation studies (Chapter 7) also showed the reappearance of Cr(VI) in Fe(II) treated soils. Based on Le Chatelliers Principle of chemical equilibrium loss of Cr(VI) from soil pore water in the presence of Fe(II) would lead to release of Cr(VI) from the sparingly soluble salts and exchange sites to maintain the thermodynamic stability constant especially when Fe(II) becomes the limiting reagent. Obviously the soil also contained huge reservoir of Cr(VI), as phosphate extractable Cr(VI).

In general the data on Mn from leachates collected from all three ports do not reflect a definitive trend and therefore its influence on oxidation of Cr(III) to Cr(VI) is likely to be minimal. While the first two days pore water ~~leachate~~ collected from the 5 cm port showed some presence of low concentrations of Mn, it may be possible that the species of Mn present could be Mn^{2+} based on the Eh and pH conditions of the system (Bricker, 1965). Amacher and Baker (1982) and Bartlett and James (1979) have reported oxidation of Cr(III) to Cr(VI) by Mn(III / IV) oxides and not in the presence of Mn(II).

The release of aqueous Ca and Cr(VI) from the 10 cm port showed a linear relationship between Ca and Cr(VI) (Fig. 8.5) and indicated that release of Cr(VI) from this contaminated soil may be controlled by a sparingly soluble source of Cr(VI). As the aqueous concentration of Ca decreased the concentration of Cr(VI) also decreased with time. Therefore, the only alternative for complete reduction of soluble Cr(VI) would be to use an excess of Fe(II) salt.

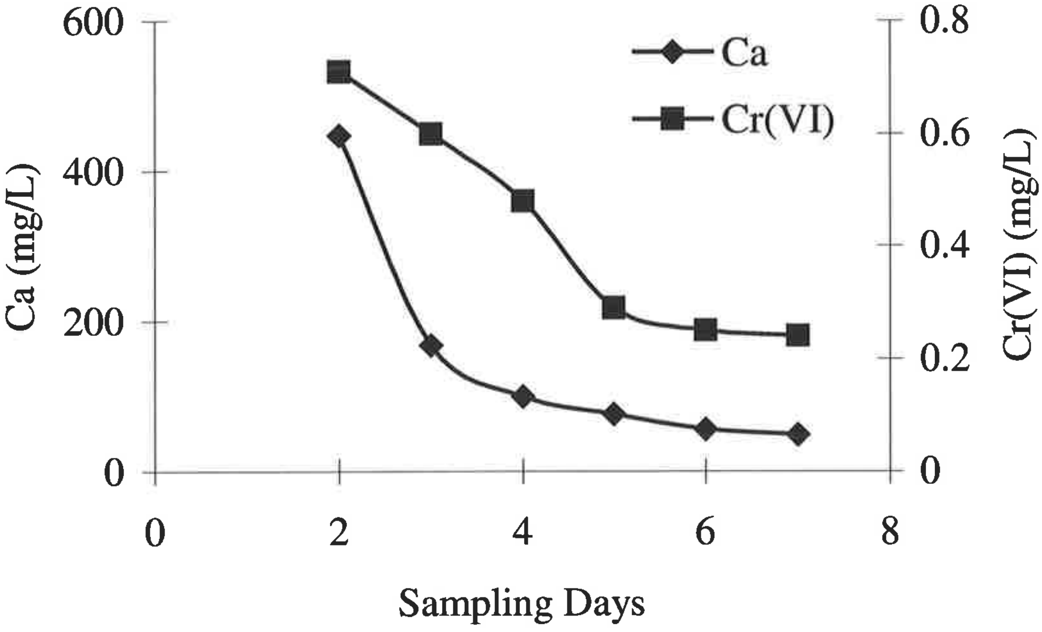


Fig. 8.5 Relationship between Ca and Cr(VI) in leachates sampled from the 10 cm port (note that the scales of the two Y axis are different)

8.2.7 Chromium Release from the Untreated Zone

The pore water ~~leachate~~ collected from the 10 cm port showed the presence of significant concentrations of water-soluble Cr(VI). This suggest that Fe(II) mixed to the depth of 5 cm was not effective in the reduction of Cr(VI) in the subsurface layer at 10 cm (Fig. 8.3). Nevertheless a gradual decrease in the concentration of water-soluble Cr(VI) from 0.7 mg/L to 0.11 mg/L was observed during 11 days of leaching.

Effluent collected from the bottom of the column at 30 cm also showed a significant release of water-soluble Cr(VI). This observation again emphasizes that Fe(II) applied up to the depth of 5 cm may not be effective for subsurface reduction of water-soluble and exchangeable Cr(VI) in this chromate contaminated alkaline soil (Fig. 8.4). However, with continued leaching a gradual and steady decrease in the release of water-soluble Cr(VI) was observed up to 60 pore volumes.

8.3 Implications of the Study and Conclusions

The results of the study demonstrated that surface incorporated Fe(II) will not effectively reduce soluble Cr(VI) present, especially in subsurface layers due to low mobility of Fe(II) and also because of the rapid reduction reaction of Cr(VI) by Fe(II). The study also implies that for effective stabilization of Cr(VI) in Cr contaminated alkaline soils, incorporation of Fe(II) in excess of 3% up to the depth (30 cm) of contamination under sufficient soil moisture conditions may be required.

The following conclusions can be drawn from the study,

- The reducing agent Fe(II) is only partially effective in stabilizing water soluble Cr(VI) in Cr contaminated alkaline soil at the rates of application. However, its effect was observed only at the zone of incorporation. This limits the practicality of the in-situ treatment.

- Higher rates of application of $FeSO_4$, in excess of 3% Fe(II), would be required for greater reduction of Cr(VI) in Cr contaminated alkaline soil.
- Depending upon the use of this land after reclamation, other options of remediation need to be considered.

CHAPTER 9

Removal of Chromate from Contaminated Water - Use of Lanthanum Salt

9.1 Introduction

In Chapters 4 through 8 an attempt was made to assess the factors that influence Cr release and mobility in contaminated soils. This chapter assesses the potential for minimizing Cr contamination of land from wastewater disposals by developing innovative techniques for removing Cr from wastewater.

Chromium (Cr) is widely used in a number of industries that generate large volumes of Cr-contaminated wastewater. With the introduction of strict environmental regulations together with the need to minimize industrial costs, most modern industries are now developing strategies to recycle metals and clean wastewater for re-use. This is generally achieved by developing primary and secondary wastewater treatment plants. Recycling the water is now considered of special urgency especially in countries with limited fresh water supplies. Available fresh water amounts to less than one half of one percent of all the water on earth. Global consumption of water is doubling every 20 years, more than twice the rate of human population growth. According to the United Nations, more than one billion people on earth already lack access to fresh drinking water. If this current trend persists, by 2025 the demand for fresh water is expected to rise by 56% and out strip currently available resources (Barlow, 1999). For these reasons and to help ensure that current water supplies will not be depleted, polluted water, including water from sludge, must be reclaimed. Such a process will provide significant impetus towards preserving limited fresh water supplies in developing countries, where serious concerns have been expressed regarding the dwindling groundwater supplies.

Amongst the industries that use Cr, leather-tanning industries are notorious for both the use of this metal and disposal of their liquid and solid waste onto productive land and water bodies. Examples of such disposals are evident in many developing countries including China and India. Both recycling of Cr and treating wastewater prior to disposal will help maintain a "clean and green" image for such industries and will safeguard our fragile water reserves. A clean and green image is critical for many developing countries that face increasing criticism from international traders for their laxed attitude towards the management of industrial wastes. Among the Cr species present in wastewater, Cr(VI) is one of the relatively more stable species and being significantly more toxic than other forms of Cr receives greater attention and is monitored by regulators throughout the world. Cr(VI) primarily exists in the forms $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ (Nieboer and Jusys, 1988) and efforts are directed to remove the toxic Cr(VI) in industrial wastewater and also from surface and groundwater contaminated with Cr(VI).

A wide array of technologies are available for the removal of chromate from wastewater. Beszedits (1988) reviewed the available treatment technologies and discussed the advantages and disadvantages of each. He reported that chemical precipitation is the most common technique used for the removal of heavy metals from wastewater. Although most heavy metals are precipitated readily by pH adjustment, Cr(VI) is highly soluble and does not precipitate from solution at any pH. Consequently, treatment of Cr contamination usually consists of a two-stage process: Step 1, the reduction of Cr(VI) to Cr(III) and, Step II, the precipitation of Cr(III). A review of the literature suggests that little research has been directed towards direct removal of chromate from contaminated waters.

Tokunaga et al., (1999) demonstrated that lanthanum (La^{3+}) salts could be used to precipitate and remove arsenite, As(III), and arsenate, As(V), from waters. They showed that La^{3+} was effective over a wide pH range and demonstrated its ability to remove As to meet the effluent and drinking water standards. Their method had the advantage of using a much smaller dose of precipitant (La^{3+}) than would otherwise be required using conventional precipitants. Like As, Cr forms oxy-anions and these often exhibit similar chemical behavior to the As analogues. It is likely therefore likely that Cr(VI) will form insoluble precipitates in the presence of La^{3+}.

9.2 Objectives

With the above hypothesis as a basis, the following objectives were set to investigate the effectiveness of a La^{3+} salt in removing Cr(VI) from waters. Specifically these objectives were;

1) to investigate the potential of La^{3+} salts for the removal of Cr(VI) from contaminated water;
2) to identify the optimum pH and molar ratio of La^{3+} to chromate for effective removal of chromate; and
3) to chemically characterize the resulting precipitates.

9.3 Materials and Methods

9.3.1 Materials

Reagent grade $K_2Cr_2O_7$ and $LaCl_3.7H_2O$ were dissolved in deionised water and used for the preparation of the respective solutions of chromate and La^{3+}.

9.3.2 Removal of Cr(VI)

A series of 50 ml solutions of 0.1 M La^{3+} (as $LaCl_3$) and 0.1 M Cr(VI) (as $K_2Cr_2O_7$) were prepared, mixed together in a beaker and stirred continually using a magnetic stirrer attached to a pH stat instrument. The pH of La^{3+} and Cr(VI) solutions at the beginning and after mixing were measured. Since the precipitation reactions were associated with a significant drop in pH, the pH was maintained via addition of 0.1 M KOH or 1 M KOH added automatically using a pH stat instrument. The pH was increased at 0.5 unit/h up to pH 12. At each point of pH, supernatant was sampled after the solutions had been equilibrated for 1h with a 10 ml syringe, filtered through 0.45 μm syringe filters and stored in polystyrene containers for La^{3+} and Cr(VI) analysis. Similarly, 50 ml solutions of 0.1 M of La^{3+} and 0.2 M Cr(VI) were mixed and studied for the removal of Cr(VI) with increasing solution pH. In order to investigate the removal of Cr(VI) at the typical waste water concentrations observed in waste water treatment plants and contaminated ground water, low concentrations of Cr(VI) (1 mM) was reacted with 1 mM, 3 mM and 5 mM of La^{3+} and the supernatant was sampled for further analysis of La^{3+} and Cr(VI).

9.3.3 Investigations on Molar Ratios of La^{3+}

For any chemical removal study it is critical to ascertain the optimum molar ratio of chemical required to remove the toxic metal from the contaminated water. It is also important that addition of La^{3+} should not itself become a contaminant of the soil and water environment. For example, Liang and Tabatabai (1977 and 1978) reported that 19 trace metals when added to soil as sewage sludge inhibited mineralization of organic nitrogen and nitrification of NH_4^+-N, which was considered to be the most important beneficial process in agricultural practice. Recently, Xu and Wang (2001) studied the effects of La and mixtures of rare earths on ammonium oxidation and mineralization of nitrogen in soil. They observed that the influence of mixtures of rare earths on potential ammonium oxidation or on N mineralization was slightly stronger in comparison with that of La^{3+}. Therefore, in the present study in order to prevent excess use of La^{3+} and also to achieve effective and complete removal of Cr(VI) from contaminated waters various molar ratios of La^{3+} and Cr(VI) were examined.

9.3.4 Determination of Cr and Lanthanum

Total soluble Cr in the supernatant and precipitate washings was determined by FAAS (the detailed procedure is discussed fully in Chapter 3). Lanthanum in solution was determined using inductively coupled plasma emission spectroscopy (ICP-AES, spectroflame modula, spectroananlytical instruments GMBH, Germany at 384.9 nm and had a detection limit of 0.044 mg/L.

9.3.5 Characterization of the Precipitate

Separate solutions of La^{3+} and Cr(VI) were combined in a beaker and stirred continually until precipitation occurred. The pH was controlled so as to give the maximum Cr(VI) removal as was observed in the earlier study (see Section 9.3.2) and 1 M KOH was delivered to attain the set pH. Solutions were left to stir for an hour after reaching the set pH and the supernatant was separated from the precipitate via suction filtration. The filtered solution was stored in polystyrene containers for La^{3+} and Cr analysis and the precipitate was washed with distilled water twenty times to remove soluble impurities, dried at 70 °C and examined by powder X-ray diffractometer (Philips PW1800 microprocessor-controlled diffractometer).

9.4 Results and Discussion

9.4.1 Removal of Cr(VI) by Lanthanum - 1:1 Molar ratio

When 1:1 molar ratios of $LaCl_3$ and $K_2Cr_2O_7$ solutions were mixed (solution pH 3.25) no precipitation was observed. A yellow precipitate started to appear with increasing solution pH. Not surprisingly, precipitation was accompanied with a significant decrease in La^{3+} and Cr(VI) concentrations between pH 4 and 5 (Fig. 9.1).

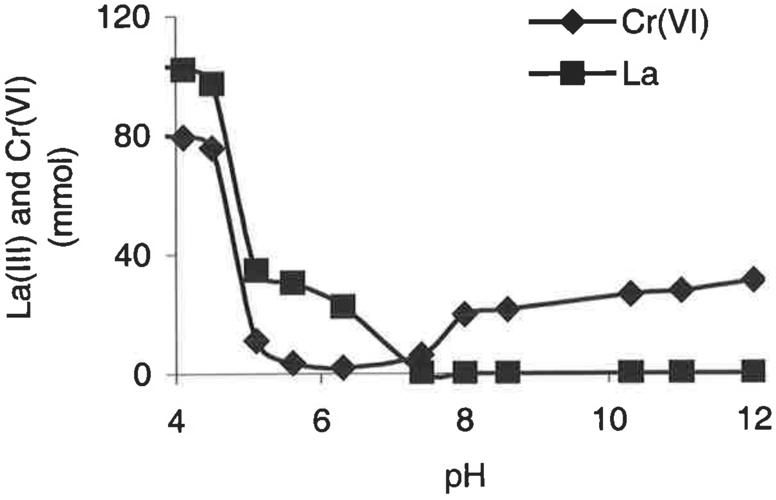


Fig. 9.1 Removal of Cr(VI) by La^{3+} as a function of pH

The maximum precipitation was observed at pH 6.3 when the solution concentration of Cr(VI) was lowest. At pH 6.3 the concentration of Cr(VI) and La^{3+} was 1.94 mmol and 22.54 mmol/L, respectively. Nearly 98% of the initial 80.8 mmol/L Cr(VI) was removed at this pH. Theoretical consideration of H_2CrO_4 dissociation suggests the predominance of H_2CrO_4 below pH 0.6, which is the first acid dissociation constant. This suggests that H_2CrO_4 is a strong acid. With increasing pH the divalent acid dissociates to the monoprotic Bronsted base, $HCrO_4^-$, which is the predominant species between pH 1 and 6; CrO_4^{2-} predominating at pH > 6.

$$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4^- \qquad Ka_1 = 10^{0.6} \qquad (1)$$

$$HCrO_4^- \Leftrightarrow H^+ + CrO_4^{2-} \qquad Ka_2 = 10^{-5.9} \qquad (2)$$

At Cr(VI) concentrations exceeding 10^{-2} M, the $HCrO_4^-$ ion dimerizes to give the dichromate ion (Equation 3),

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow 2HCrO_4^- \qquad K = 10^{-2.2} \qquad (3)$$

Hence, based on the dissociation constants and dimerization of chromate the dominant chromate species present in the initial chromate solution used for precipitation would be $Cr_2O_7^{2-}$ and $HCrO_4^-$. Speciation calculations using MINTEQA2 (1995) suggest that 61% of the Cr is present as $Cr_2O_7^{2-}$ and 39% is present as $HCrO_4^-$ in the initial Cr(VI) solution. No precipitate was observed when La^{3+} solution was mixed with Cr(VI) solution at this pH. Although some precipitation was observed when the pH was increased to 4.5, a significant removal of Cr(VI) and precipitation was observed at pH 5.1. At this pH MINTEQA2 predicted an increase in the chromate ($HCrO_4^-$) species

(42.1%) and a relative decrease (55.2%) in the dichromate ($Cr_2O_7^{2-}$) species in solution. Further at pH 6.3 when maximum removal of Cr(VI) occurred the dominant chromate species predicted was $HCrO_4^-$ (57.2%) and only 2.4% $Cr_2O_7^{2-}$ was found in the solution. Based on maximum removal of Cr(VI) from the solution at pH 5 – 6 it is most likely that La^{3+} precipitates chromate as La-$HCrO_4^-$ compounds rather than as La-$Cr_2O_7^{2-}$. The precipitation reaction at the maximum removal pH of 6.3 can be expressed as follows:

$$2La^{3+}_{(aq)} + 3HCrO_{4\,(aq)}^{-} \rightarrow La_2(CrO_4)_{3(s)} + 3H^{+}_{(aq)} \qquad (4)$$

A significant observed drop in pH associated with the precipitation reactions also supports the above chemical reaction. The consumption of OH^- ions was high at pH 4.5 – 6 relative to that above pH 6.5 indicating acid was being produced in at the lower pH range. Another possible reaction above pH 6 could be with the dominant chromate species of CrO_4^{2-} as follows:

$$2La^{3+}_{(aq)} + 3CrO_{4\,(aq)}^{2-} \rightarrow La_2(CrO_4)_{3(s)} \qquad (5)$$

The precipitation of $La_2(CrO_4)_3$ was supported by the X-ray diffraction (XRD) patterns of the purified precipitates separated at pH values exceeding 12. The XRD pattern shown in Fig. 9.2 match the reference material, $La_2(CrO_4)_3$ (Leppa-Aho and Valkonen, 1994). In the acidic pH range (4.5 – 6.3) removal of Cr(VI) took place coincidentally with the decrease in residual La^{3+} concentrations where La^{3+} ions do not hydrolyze. In the alkaline pH range, 7.4 – 12, residual Cr(VI) concentrations increased with increasing pH whereas residual La^{3+} concentrations remained low due to hydrolysis of La^{3+}.

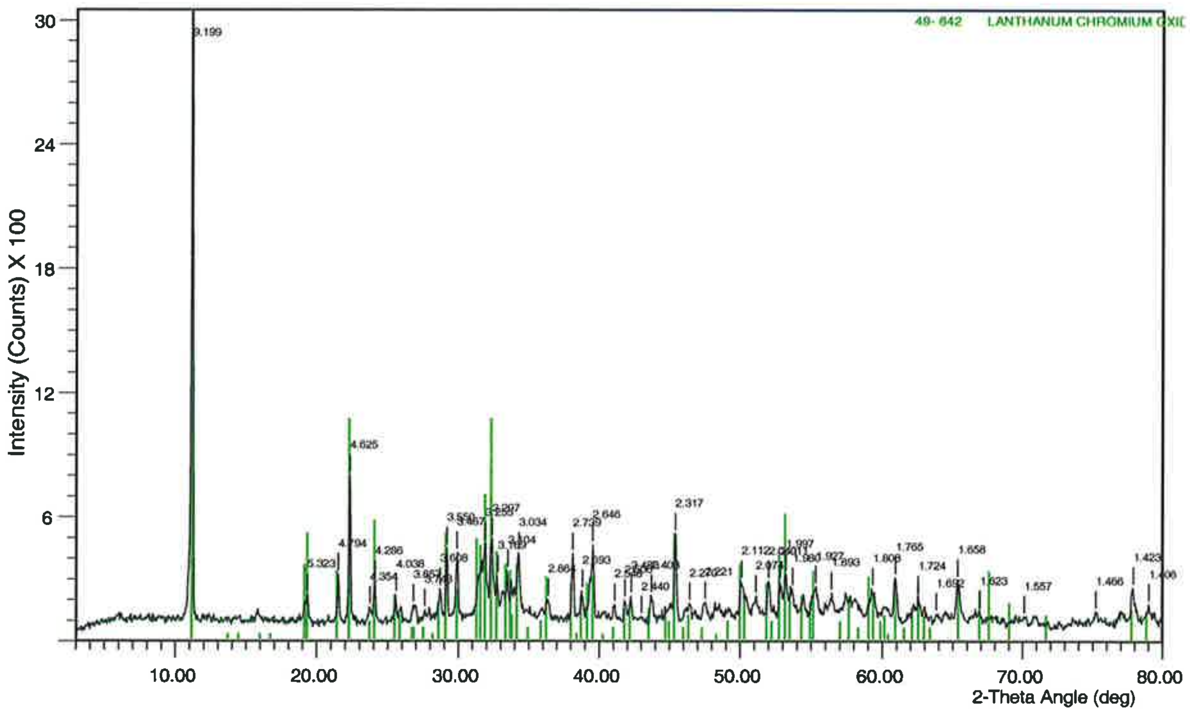


Fig. 9.2. XRD pattern of the precipitate matching the reference material $La_2(CrO_4)_3.7H_2O$ at the bottom

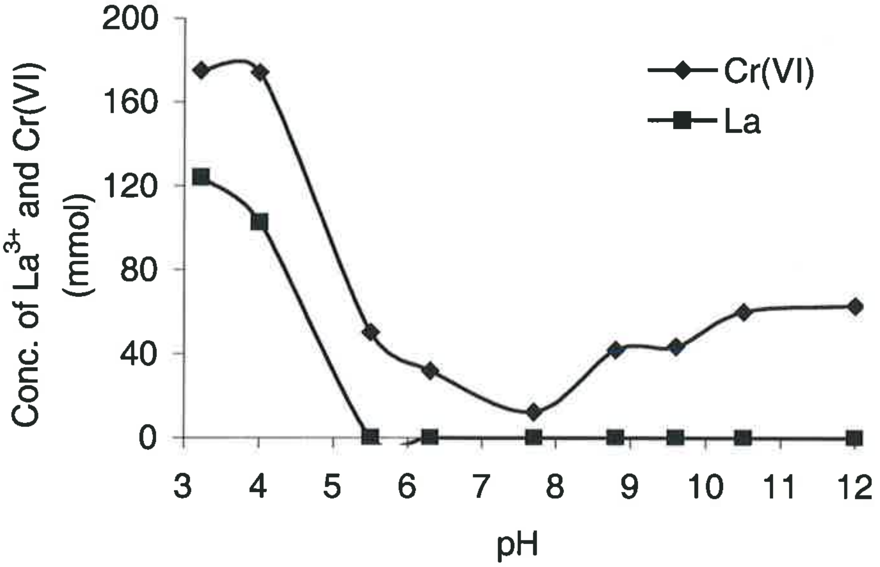


Fig. 9.3 Removal Cr(VI) by lanthanum as a function of pH at 1:2 ratio

9.4.2 Removal of Cr(VI) by Lanthanum - 1:2 Molar Ratio

A similar precipitation pattern to that observed at a 1:1 mole ratio of La^{3+}:Cr(VI) was observed for the mixing of equivolumes of 0.1 M La^{3+} and 0.2 M Cr(VI). Initially the pH of the La^{3+} and Cr(VI) solution mixture was 3.22 and no precipitation was observed. Once the pH exceeded 5.5 by the addition of KOH, a dense yellow precipitate started to appear.

Fig. 9.3 shows that the concentrations of Cr(VI) and La^{3+} in the supernatant solution dropped to 50.35 mM and 0.13 mM from 175.1 mM and 124.2 mM respectively at pH 5.5. The maximum removal of Cr(VI) was observed at pH 7.7 slightly later than was observed in the earlier experiment with a 1:1 mole ratio of La^{3+} and Cr(VI) (pH 6.3). This may be due to the lower proportion of free La^{3+} ions observed in solution at pH exceeding 5.5 when the maximum precipitation of Cr(VI) occured. The earlier disappearance of La^{3+}, compared to the 1:1 mole ratio run, may be attributed to exceedance of the solubility product of La-Cr compounds due to the higher Cr(VI)-La^{3+} concentrations used or to possible loss of free La^{3+} through hydrolysis. MINTEQA2 calculations suggest the presence of higher percentages of $Cr_2O_7^{2-}$ (16.3%) for 1:2 ratio at pH 6.3 compared to only 2.4% $Cr_2O_7^{2-}$ at a 1:1 ratio and support the shift in equilibrium towards complex precipitation. At the point of maximum Cr(VI) removal, Cr(VI) concentration in solution was 12.4 mM, indicating 93% removal of Cr(VI) was achieved, compared to 98% removal for the 1:1 mole ratio run. XRD characterization of the precipitate recovered above pH 12 showed the same diffraction pattern as $La_2(CrO_4)_3.7H_2O$. This compound was also observed in the 1:1 run and suggested that the same chemical reactions observed there was also in operation for the 1:2 run.

9.4.3 Removal of Lower Concentrations of Cr(VI)

The effectiveness of La^{3+} to immobilize C(VI) from contaminated water was examined using solutions containing 1 mM concentration of Cr(VI). The results are shown in Figs 9.4, 9.5 and 9.6. At low Cr(VI) concentrations when an equivalent amount of La^{3+} (0.5 mM) was added, there was no change in Cr(VI) concentration until the solution pH was raised to between 6.7 and 7.6 (Fig. 9.4). Even at this pH, only 18% of the chromate was removed. This suggested that La^{3+} was the limiting reagent and that the ionic product of the compound did not exceed the solubility product. Increasing the La^{3+} concentration to 1.5 mM increased the efficiency of Cr(VI) removal to 53% and the concentration of Cr(VI) decreased in the pH range of 6.8 to 8.8 (Fig. 9.5). When the initial La^{3+} concentration was further increased to 2.5 mM significant removal of Cr(VI) was observed (99%) and the lowest concentration of 0.008 mM was achieved at pH 8.5 (Fig. 9.6). Coinciding with the removal of Cr(VI), La^{3+} concentrations also started to decrease from pH 7.5 and continue to decrease up to pH 11.5. At pH > 9 the loss of La^{3+} in solution would be due to La^{3+} hydrolysis. At high pH (> 9) the concentration of Cr(VI) started to increase in all experiments but there was no corresponding increases in La^{3+} which would have suggested complex dissolution. Tokunaga et al. (1999) reported similar observations for low concentrations of As(V) removal by La^{3+}. The optimum pH range for effective removal of low concentrations of Cr(VI) was 7.5 – 8.5. Adjusting the initial chromate:La^{3+} ratio to greater than 1:5 reduced the residual chromate concentrations to a level that met both the effluent and drinking water standards.

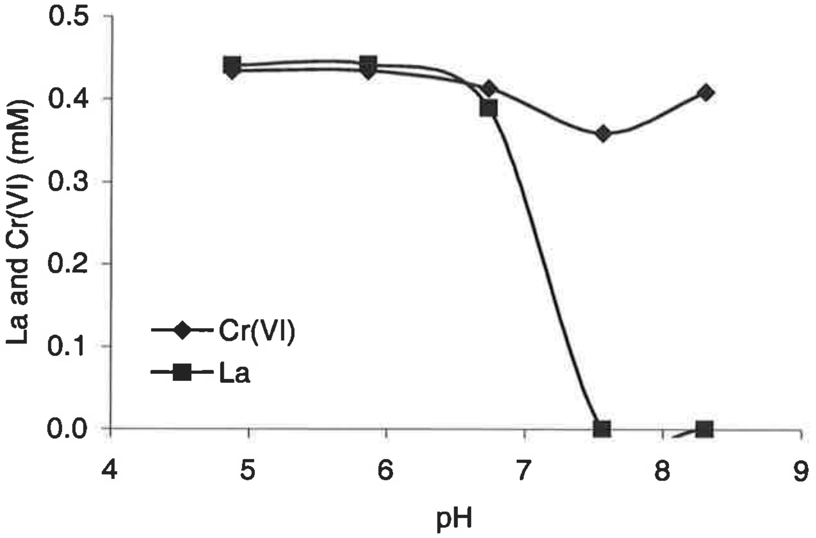


Fig. 9.4 Removal of Cr(VI) by lanthanum as a function of pH at equal ratio of La^{3+} and Cr(VI)

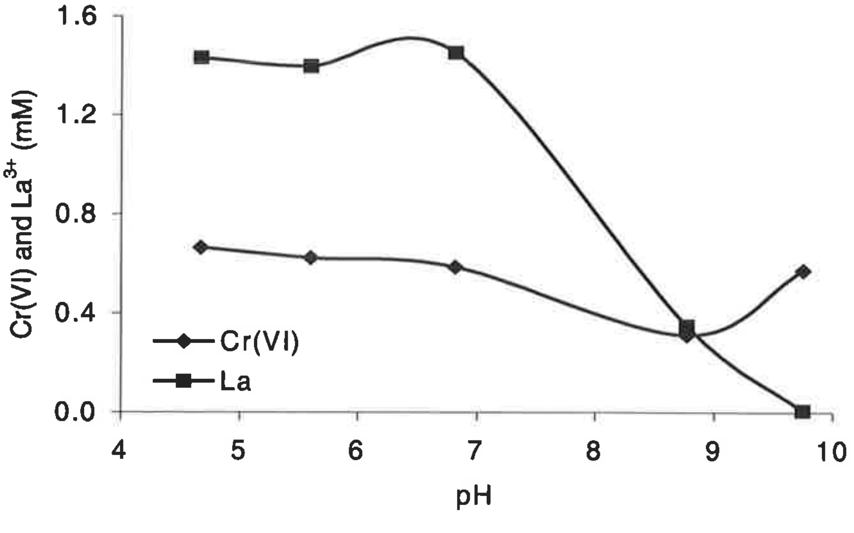


Fig. 9.5 Removal Cr(VI) by La^{3+} as a function of pH at 1:3 ratio of Cr(VI) and La^{3+}

9.4.4 Kinetics of Cr(VI) Removal by La^{3+}

A kinetic study was conducted by mixing 0.1 M Cr(VI) (50 ml) and 0.1 M La^{3+} (50 ml). The initial pH of the mixed solution was 3.8 and pH was allowed to rise to 6.3 with the addition of 0.1 M KOH and continual stirring. The pH of 6.3 was chosen because this was the pH of optimum precipitation. Once the solution attained the desired pH (6.3) the supernatant was sampled at 0; 5; 15; 30; 60; 120; 240; 480; 720 and 1440 minutes to investigate the removal of Cr(VI) and La^{3+} from the solution. The results indicated that at t = 0, 95% of Cr(VI) and 94% of La^{3+} was removed from solutions (Fig. 9.7).

Therefore the precipitation reaction was virtually instantaneous, since 95% of Cr(VI) was removed from the system at t = 0. i.e. immediately upon mixing the two solutions. The amount of Cr(VI) removed from the solution increased by only 1% (to 96%) after 240 min and there was virtually no change in the solution concentration of Cr(VI) after this time; indicating solubility equilibrium between the solid and the solution had been obtained. The precipitate thus obtained was washed with distilled water, dried and characterized using X-ray diffraction studies. The XRD showed a pattern identical to that of the earlier studies at 1:1 and 1:2 Cr:La mole ratio indicating that $La_2(CrO_4)_3.7H_2O$ was again the reaction product. At higher initial Cr(VI) concentrations a pH of 6.3 would be effective in the complete removal of Cr(VI) from solutions. However, at lower initial Cr(VI) concentrations pH range of 7.5 to 8.5 would be more suitable for complete removal of Cr(VI). In general the pH range of 6 – 8.5 would seem to be favorable for the removal of Cr(VI) by La^{3+} as a $La_2(CrO_4)_3$ precipitate.

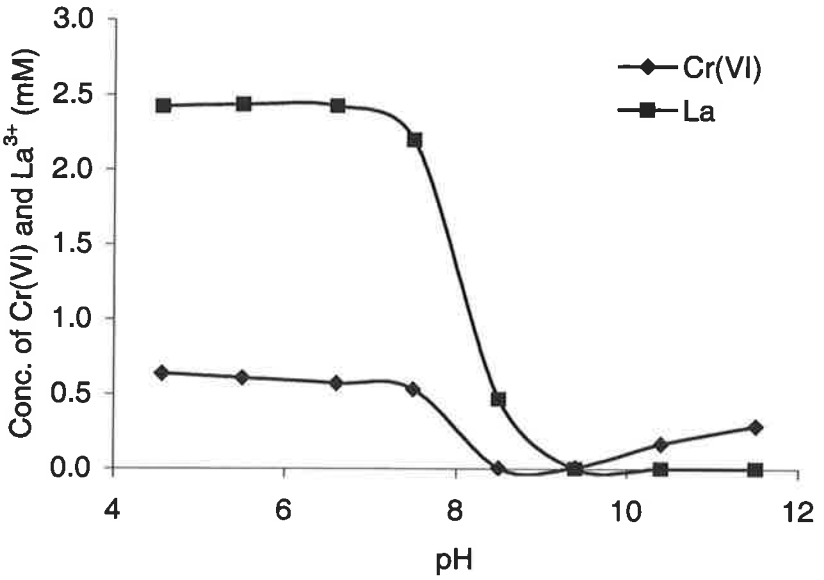


Fig. 9.6 Removal of Cr(VI) by La^{3+} as a function of pH at 1:5 ratio of Cr(VI) and La^{3+}

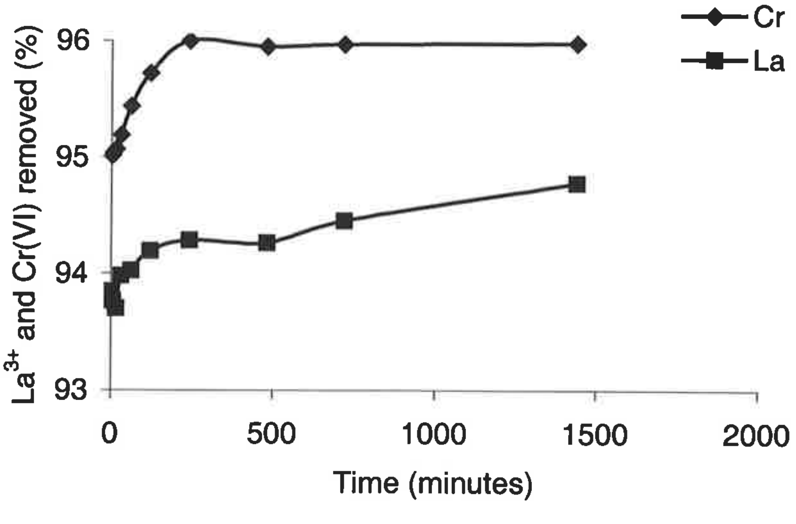


Fig. 9.7 Removal of Cr(VI) and La^{3+} as a function of time

The results of effective removal of Cr(VI) by La^{3+} both at high and low Cr(VI) concentrations relevant to waste water and contaminated waters suggests that La^{3+} can be potentially used to remediate Cr rich waste water generated by industries and Cr contaminated well water in the vicinity of tannery industries. However, further studies are required to investigate the efficiency of Cr(VI) removal by La^{3+} in the presence of other dissolved ions that may be present in industrial waste and groundwater.

9.5 Conclusions

Based on the above study following conclusions were drawn.

- Lanthanum chloride was effective in removing Cr(VI) from solutions as a $La_2(CrO_4)_3.7H_2O$ precipitate.
- At high initial concentrations of Cr(VI) (0.1 M), Cr(VI) removal was 98% at 1:1 mole ratio and removal was 93% for 1:2 mole ratio of La^{3+} and Cr(VI).
- More La was required to remove Cr(VI) at low initial concentration of Cr(VI) (1 mM). The ratio of 5:1 of La^{3+}:Cr(VI) effectively removed 99% of Cr(VI) from solutions.
- The optimum pH for Cr(VI) removal by La^{3+} was 6.3 for high initial concentrations of Cr(VI) and a pH range of 7.5 – 8.5 was effective in removing Cr(VI) from low initial concentrations of Cr(VI). In general the pH range of 6 – 8.5 was found to be ideal for complete removal of Cr(VI) from solutions by La^{3+}.

Chapter 10

Summary and Conclusions

This chapter summarizes the key research outcomes arising from the present study and key research issues that need further consideration.

Numerous investigators have conducted extensive studies on the fate and behavior of Cr in the soil environment (Chapter 2). However, most of these studies have focused on freshly contaminated soils and the outcomes from such studies may not bear any relevance to long-term contaminated soils. Unlike freshly contaminated soils, in which contaminant bioavailability is high, long-term contaminated soils show significant decline in bioavailability with time. Some researchers have attributed this decline in bioavailability to the diffusion of contaminants into micropores making desorption difficult and therefore a slow process. This effect of aging may also be applicable to tannery waste contaminated sites that not only contain high levels of Cr but also contain high levels of other soluble salts and organic compounds (Naidu et al., 2000a). The influence of soluble salts on the mobility of Cr (adsorption and desorption), the effect of aging on partitioning of Cr in different soil fractions and viable options to remediate the long-term tannery waste contaminated site at Mount Barker were all examined in this present study.

Since Cr can exist in a number of different forms, in particular Cr(III) and Cr(VI), an attempt was made to develop a sensitive and rapid analytical technique for speciating soluble Cr using capillary electrophoresis. Capillary zone electrophoresis

(CZE) was considered in favour of existing ion chromatography techniques because of it's rapid separation and low analysis cost.

Using CZE, Cr(III) was simultaneously determined together with Cr(VI) in a single run by chelating Cr(III) to form anionic complexes. The complexing ligands considered included, Nitrilotriacetic acid (NTA), N-2-hydroxyethylethlendiaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), and 2,6-pyridinedicarboxylic acid (PDCA). The results of this work (Chapter 3) demonstrated that 2,6-PDCA can be used as a derivatizing agent for Cr(III) and is a useful ligand for the determination of chromium speciation using CZE with direct UV detection. The derivatization conditions, such as solution pH and the concentration ratio (M/L) were both important for the formation of a single stable $[Cr(PDCA)_2]^-$ complex. The proposed method offers high separation efficiency and short analysis time in comparison with conventional spectrophotometric methods. However, it was found that the detection limits of CZE were higher (100 μg/L) than the detection limits of Ion Chromatography methods (< 10 μg/L). As stacking was not possible with the instrument used during this study, it was not feasible to enhance the sensitivity of CZE to estimate Cr(VI). For this reason, IC was selected for all aqueous speciation of Cr(VI) (USEPA, 1996). However, CZE speciation of Cr remains an excellent technique for wastewaters containing elevated levels of Cr and the technique would also be even more useful in conjunction with equipment having facilities for sample stacking.

Following this initial study which focused on Cr speciation techniques, the research was subdivied into (a) an initial assessment of the contaminated soil for total and soluble Cr and based on these results further detailed investigations on (b) factors that control Cr desorption in contaminated soils and options for minimizing desorption. An effort was also made to investigate the nature of binding by mineral and organic pools comprising the contaminated soils.

In the long-term tannery waste contaminated site at Mount Barker total Cr concentration exceeded 9% in the surface horizon (0 - 15 cm) and 0.05% in the subsurface horizon (50 - 90 cm). Detailed sequential fractionation studies presented in Chapter 4 revealed that more than 91% of the total Cr was associated with the H_2O_2 extractable organic fraction in the surface layer. These results were consistent with similar observations made by other laboratories for Cr contaminated organic rich soils (Dudka and Chlopecka, 1990; Milacic and Stupar, 1995; Maiz et al., 1997; Zufiaurre et al., 1998; Fernandez Albores et al., 2000).

However, none of these published studies had investigated the nature of binding between Cr and organic matter. In the present study, we investigated the nature of Cr-organic matter interactions using solid state ^{13}C CP/ MAS NMR. T_1H relaxation rates with contaminated surface soil (top soil), HF treated soil from the surface layer, sludge separated from soil of the surface layer and collagen amended Cr(III) samples confirmed that strong binding of Cr with organic matter was occurring in the contaminated site. The average T_1H relaxation rates for top soil, HF treated top soil, sludge and collagen amended with Cr(III) samples were 10.5, 8.9, 11.3 and 7.4 ms respectively. The especially good correlation between the T_1H relaxation rates observed for HF treated surface soil and collagen amended with Cr(III) samples clearly indicated the binding strength of Cr to organic material even after the harsh HF treatment of the surface soil. The solid state ^{13}C CP/ MAS NMR study also revealed that the NMR spectra of the three samples were very similar to that of collagen (Smernik and Oades, 2000a), indicating a predominance of protein structures of the organic wastes present in the contaminated site.

As was observed with the soil from the surface layer, Cr from the subsurface layer was also predominantly partitioned into H_2O_2 extractable organic-bound fraction (45.3%). However, equal proportions of Cr were partitioned in the residual fraction of the soil from subsurface layer.

Water-soluble (0.004%) and phosphate exchangeable (0.01%) fractions of Cr in the soil from the surface layer were low compared to other fractions. Although water soluble and exchangeable fractions were very small, aqueous speciation of Cr showed that Cr(VI) was the predominant species released in both of these fractions. Both water soluble and phosphate extractable Cr exceed the USEPA permissible limits (0.05 mg/L) for water indicating the potential for Cr(VI) migration into the subsurface environment and eventual contamination of the groundwater aquifer at the site (Naidu et al., 2000b).

However, speciation of Cr in water soluble and phosphate exchangeable fractions in soil from the subsurface layer showed a predominance of Cr(III) in the extracts. This suggested that subsurface reduction of Cr(VI) to Cr(III) had occurred. Nevertheless lateral movement of water can assist migration of toxic Cr(VI) from surface layer to surface and groundwater resources at the site which has a slope $>30^o$. The presence of large concentrations of exchangeable Cr(VI) indicated that a potentially large source of Cr was bioavailable over a long period of time at the site. This was not surprising given the large amount of total Cr present at this site (9%); where some of this Cr is likely to be present as sparingly soluble Ca-salts (Chapter 5). Additionally, mineralisation of organic matter could mobilize Cr associated with that organic matter (Ure and Davidson, 1995).

The presence of large concentrations of Cr in the soil and also in the soil water extracts led to further investigations focusing on factors that enhanced Cr release from the contaminated soils. Thus Chapters 5 and 6 investigated the effect of soil solution composition on the mobility of Cr in the surface and subsurface contaminated soil. Since tannery wastes generally contain elevated concentrations of Na^+, Ca^{2+}, Cl^-, SO_4^{2-} and PO_4^{3-} (UNEP and IEO, 1991), the effects of solution cations, Ca^{2+} and Na^+, of similar ionic strength and anions, chloride and various concentrations of phosphate, on the desorption behaviour of Cr was studied.

Following preliminary studies, a 2 h desorption and a 20:1 solution:soil ratio were chosen for all subsequent studies. The pH of the soil samples ranged from 7.9, in the surface 50 cm, to 3.9, in samples from below 50 cm depth. The strongly acidic nature of the soils below 50 cm was surprising since such an increase in soil acidity with depth had not been previously reported in duplex soils around Adelaide. Generally, duplex soils are typified by a loamy and acidic surface horizon overlaying a dense sodic (pH > 7) layer (Northcote and Skene, 1972). Detailed SEM examination of the soil samples from the subsurface layer revealed highly weathered framboidal particles with morphology similar to that of pyrites. It was likely that the strongly acidic nature of the soil from the subsurface layer was due to the weathering of pyrites in which SO_4^{2-} and H^+ ions were released. This was supported by the high sulphate concentration recorded in the acidic subsurface soils.

Aqueous speciation of Cr in soil water extracts showed a predominance of Cr(VI) species from soil in surface and Cr(III) in subsurface layers. The rapid desorption of water soluble Cr(VI) from soil in alkaline surface layer were similar to the observations reported by Kookana et al., (2000). The initially rapid and subsequently slow release of Cr(VI) in excess of 10% of the total Cr(VI) present in the soil to water extracts from surface soil (pH 7.9) illustrated the potential for slow but continued Cr loading of subsurface soil from vertical leaching of this mobile Cr fraction. In contrast to the soil from the surface layer, release of < 0.2% of the total Cr in the acidic soil from subsurface layer (pH 3.9) was not significance in the potential migration of Cr.

The successive batch desorption of the contaminated soil from surface and subsurface layers (Chapter 5) with 0.01 M $CaCl_2$ and 0.03 M NaCl showed contrasting effects of index cations on the desorption of Cr. In the alkaline soil from the surface layer, Cr release decreased with increasing cationic charge (water $\geq Na^+ > Ca^{2+}$) while the trend was reversed ($Ca^{2+} > Na^+ >$ water) in acidic soil from the subsurface layer. In alkaline soil the presence of Ca^{2+} in the system favoured greater retention and lesser mobility of Cr(VI) when compared to the Na^+ system. The decrease in Cr(VI) desorption in the presence of Ca^{2+} was attributed to hydronium ion (H^+), due to the marked decrease in solution pH and/or to the changes in the thickness of the diffuse double layer and possibly the reduction of Cr(VI) to Cr(III) under high organic and acidic conditions. The other possibility was that CrO_4^{2-} might simply have precipitated as $CaCrO_4$ because of the excess Ca^{2+} added to the contaminated soil, which already had higher Ca^{2+} concentrations than normal soils. Indeed, detailed examination of the mineralogy of the soil samples from surface layer using both XRD and SEM revealed the presence of large amount of calcite (15%). In acid soils cationic competition may desorb and facilitate migration of Cr(III). Both pH and the nature of Cr appear to play a significant role in desorption process in the presence of electrolytes.

Phosphate at concentrations > 1.6 mmol/L, increased the amount of Cr(VI) desorbed from soil in the surface layer. Since both chromate and phosphate are adsorbed by similar specific adsorption mechanisms it was not surprising to see enhanced release of Cr(VI) by phosphate (Bartlett and James, 1988). This effect was enhanced in the presence of Na^+ than Ca^{2+}. Phosphate at a concentration of 3.2 mmol/L in both electrolytes desorbed nearly 85% Cr(VI) compared with the phosphate free system, and significant correlation between phosphate adsorption and chromate desorption was observed in the contaminated soil from the surface layer.

The batch techniques used in Chapter 5 represented a close system, the desorbed species were not removed from the sorbing environment and therefore the products accumulated in the system. The retained reaction products could influence processes and their interpretation because reactions may not be unidirectional and reverse reactions are often not considered. Desorbed species may also cause secondary reactions – for example, precipitation (Sparks, 1989; Amacher et al., 1990). Therefore, in Chapter 6, desorption of Cr from the long-term contaminated soil from surface layer (0 - 15 cm) was studied using a repacked column to better simulate the field conditions by addressing some of the inherent problems highlighted above for batch studies.

Influent solutions with similar ionic strength of Ca^{2+} and Na^+ were leached in sequence through the contaminated soil collected from the surface layer that had been packed in a glass column. The soil was packed in the column to the same bulk density as that observed in the field. 3 mmol/L $H_2PO_4^-$ (KH_2PO_4) solution was also leached through the soil column to investigate the effect of phosphate on Cr(VI) desorption from the contaminated soil. For comparison with the different electrolytes deionised water was also leached through the soil column and an initially rapid and subsequently slow release of Cr(VI) was observed. This was consistent with the results observed during the batch desorption studies. Thermodynamically the dominant chromate species present in the high pH soils was expected to be CrO_4^{2-}. Its association with other salts in the soil determined the solubility of Cr (VI) in solution. In the soil used in this experiment, Cr

(VI) may have been associated with moderately soluble $CaCrO_4$ and this could be one reason for the continued slow release of Cr (VI) through out the study (Nieboer and Jusys, 1988). A total of 9.21 mg/kg of Cr (VI) was released in 24 pore volumes (PV) out of a total 40 mg/kg Cr (VI) present in the contaminated soil. The concentration of Cr (VI) released at 24 PV was significantly higher (0.3 mg/L) than the maximum permissible level for Cr (VI) in natural water. The ready desorption of Cr was not surprising given the presence of Cr (VI) in the contaminated surface soils (Avudainayagam et al., 2001). It was expected that the alkaline soil pH would inhibit anion adsorption especially in soils with high net negative surface charge.

In both leaching studies there was a sharp drop in the release of Cr(VI) whenever Ca^{2+} was leached through the soil column. For example, the concentration of Cr(VI) decreased sharply from 0.7 mg/L at one PV to 0.3 mg/L at 3 PV compared to a gradual decrease in the concentration of Cr(VI) to 0.5 mg/L at the same stage when only deionised water was leached through the contaminated soil column. Coinciding with the decrease in release of Cr(VI), the effluent pH also decreased by 0.2 unit during Ca^{2+} leaching. However, when Ca^{2+} was replaced with Na^+, the amount of Cr(VI) desorbed increased with each additional PV of the electrolyte and reached a maximum concentration of 0.36 mg/L. During Na^+ leaching the effluent pH again increased by 0.2 units. So consistent with the observations in batch desorption studies, column leachings results confirmed the effect of Ca^{2+} on retention of Cr(VI) and Na^+ on enhanced desorption of Cr(VI) from this contaminated soil of the surface layer. As stated in batch desorption studies, the decrease in Cr(VI) desorption in the presence of Ca^{2+} may be attributed to either adsorption of CrO_4^{2-} which is favoured by the decrease in pH and/or to the changes in the thickness of the diffuse double layer. The pH increase during Na^+ would have favoured desorption of anionic Cr(VI) from the exchange sites.

To further confirm the effect of Ca^{2+} batch desorption experiments were conducted using varied concentrations of Ca^{2+} (0.001 M, 0.002 M, 0.003 M, 0.01 M and 0.05 M). The results revealed that there was a significant decrease in desorption of Cr(VI) as the concentration of Ca^{2+} was increased. This confirmed that the presence of Ca^{2+} in soil solution favoured higher retention of Cr(VI) in the contaminated surface soil environment.

The enhanced release of Cr (VI) in the presence of phosphate ligands at concentrations > 3.0 mmol/L was also confirmed in batch desorption experiments. Moreover, this study revealed that the presence of Ca^{2+} at saturated concentrations in the tannery contaminated soils induced the formation of calcium-phosphate phases and decreased the ionic activity of phosphate. It was obvious from these results that a considerable amount of water soluble and exchangeable Cr(VI) was present in the surface layer of the contaminated soil and that remedial measures would be required to prevent migration of toxic Cr(VI) from the surface layers to the subsurface and subsequently to groundwater resources.

Therefore, in Chapter 7 and 8 chemical remediation options were investigated to devise strategies for the decontamination of toxic Cr(VI) present in the surface layer of the contaminated site. Among the reducing agents with the greatest potential to reduce toxic Cr(VI) to non toxic Cr(III), inorganic Fe(II) is often found to be the best reducing agent, by promoting the formation of Cr(III) solids of low solubility (Sass and Rai, 1987). Moreover, the formation of a solid Cr(III) phase greatly diminishes the potential for transformation back to Cr(VI) (Fendorf et al., 1992).

Preliminary batch and incubation studies were carried out to optimize the dose of Fe(II) necessary to reduce water soluble and exchangeable Cr(VI) in this highly contaminated soil from surface layer (0 –15 cm) and to investigate the stability of remediation technology under wet-dry cycles similar to that observed in the field. Initially the kinetics of Cr(VI) reduction by Fe(II) was studied under batch system using low and very high doses of Fe(II). $FeSO_4$ was added as the source of Fe(II). The tubes were removed at time intervals of 0.5, 1, 5, 7, and 24 h and the Fe(II) doses imposed were 0, 0.1, 0.2, 0.5 and 10% (on soil weight basis). After equilibrating the dry soil with Fe(II), deionised water was first used as an extractant to study the effect on water soluble Cr(VI) and thereafter, in the same soil residue, 10 mM phosphate buffer (K_2HPO_4/KH_2PO_4 – pH 7.2) was added as an extractant to examine the reduction in exchangeable Cr(VI).

The result of the kinetic study showed that at any given time, Cr(VI) reduction was rapid and that increasing levels of Fe(II) increased the reduction of water-soluble Cr present in the soil. This effect of Fe(II) was also observed for exchangeable Cr(VI). The results are consistent with similar observations reported by James (1994) for reduction of Cr(VI) by Fe(II) in Cr ore processing residue contaminated soils. However, in this study, the data also showed that the amount of total soluble Cr increased with the duration of equilibration, suggesting that for complete desorption of Cr(VI) equilibration periods exceeding 30 min may be needed. However, mixing high $FeSO_4$ did not show a definitive trend for total soluble Cr. A significant reduction of total soluble Cr was observed for the 0.5% and 10% of $FeSO_4$ treatments when compared to the control at 30 min equilibration. The reduction of water-soluble Cr was nearly 85% and 100% for 0.5% and 10% of $FeSO_4$ respectively. According to Eary and Rai (1988) the overall reaction of Cr(VI) reduction by Fe(II) was complete within 1 – 2 minutes. In the present study the shortest time observed for Cr(VI) reduction in the soil was 30 min. In general, increasing levels of Fe(II) increased the reduction of phosphate exchangeable Cr in the contaminated surface soil. A significant reduction was observed in the 0.5% (85%) and 10% (100%) $FeSO_4$ treated soils compared to the control. Complete reduction of water soluble and exchangeable Cr(VI) was observed for the high dose of 10% Fe(II) treated soils. However, the treatment resulted in a brown precipitate, indicating the formation of Fe(OH)x compounds and possible loss of Fe(II) from the pore water. This precipitation was accompanied by a significant decrease in soil pH.

In the next set of batch experiments optimization of the Fe(II) dose required to completely reduce water soluble and exchangeable Cr(VI) (control, 1, 2.5, 5 and 7.5% on soil weight basis) was investigated after 24 h equilibration. Reduction of 90 – 100% of the water soluble and exchangeable Cr(VI) occurred with an increase in Fe(II) loading from 1% $FeSO_4$ (on soil weight basis) to the 7.5% compared to the control. Under ideal conditions and in pure systems, 3 moles of Fe(II) are stoichiometrically required for complete reduction of a 1 mole of Cr(VI) to Cr(III). The curvilinear relationship between Fe(II) and Cr(VI) observed in this study suggests some loss of Fe(II) from soil pore water to reactions other than Cr(VI) reduction. Loss of Fe(II) in the soil is possible through sorption, complexation by organics and oxidation by atmospheric O_2. These reactions may therefore limit the effective reduction of Cr(VI) by Fe(II). Thus, in this highly contaminated soil, more Fe(II) was consumed for complete reduction of Cr(VI). With an increase in Fe(II) loading beyond 2.5% a brown precipitate was observed indicating the formation of Fe-(OH)x compounds. However, no drastic pH decrease was observed for 2.5% Fe(II) treatment when compared to the control soil.

In incubation studies the optimized dose of Fe(II) (1 – 2.5% $FeSO_4$), which had been calculated under batch conditions, did not completely reduce the water-soluble and exchangeable Cr(VI) under a soil moisture content fixed at 50 % field capacity. Although an initial reduction of water-soluble and exchangeable Cr(VI) in the $FeSO_4$ incubated soils was observed eventually Cr(VI) reappeared. Given that Fe(II) loading in these soils exceeds the minimum concentration needed for complete reduction of labile Cr(VI) the reappearance of Cr(VI) may also suggest loss of Fe(II) either via ion exchange process or via oxidation of Fe(II) to Fe(III)(OH) which is an insoluble compound. Another possibility for the reappearance of Cr(VI) could be the oxidation of reduced Cr(III) by MnO_2 that may be present in the contaminated soil. Results for water-soluble Cr(III) indicated the presence of soluble Cr(III) in the first 2 days of incubation irrespective of the $FeSO_4$ treatments. However, in our laboratory, the redox potential of freshly spiked Cr(III) and Cr(VI) to the contaminated surface soil showed a low oxidation potential for spiked Cr(III) (0.2 – 0.3%) and high reduction potential for spiked Cr(VI) (85%). The dry cycle significantly increased the concentrations of exchangeable Cr(VI) in this contaminated soil. The rate of desorption of Cr(VI) and/or solubility of Cr(VI) in this contaminated soil could be a limiting factor for complete reduction of water-soluble Cr(VI) by Fe(II).

The results from the laboratory incubation studies were used as a basis for an investigation of the potential for remediating Cr(VI) in the contaminated soil using an intact core collected from the contaminated site as these better approximate field conditions. The specific objective was to assess the effectiveness of surface mixed $FeSO_4$ for reduction and stabilization of chromate present in the surface and subsurface layers at the contaminated site (Chapter 8). A high dose of Fe(II) salt (3% on soil weight basis) was used to achieve complete reduction of Cr(VI) in the surface soil and also for reduction of Cr(VI) present in the subsurface soil due to migration. Two sampling ports were installed down the core profile to collect samples immediately below the Fe(II) treated layer and the layer thereafter.

Analysis of effluent samples taken from directly below the Fe(II) treated layer (5 cm) indicated that the $FeSO_4$ treatment had dramatically reduced the pore water Cr(VI) concentration. This equated to nearly 95% reduction of the soluble Cr(VI) in Fe(II) treated zone compared to the untreated zone. Therefore, the pore water from the treated zone showed initially low Cr(VI) concentrations. As leaching progressed, fresh Cr(VI) was released from the aggregates and was not reduced due to the lack of available Fe (II). The increase in Cr(VI) concentration with time probably indicates the gradual oxidation of Fe(II) to Fe(III) during Cr(VI) reduction. Obviously the soil contained a very large reservoir of Cr(VI) (The concentration of phosphate extractable Cr(VI) was 10 mg/kg). The pH of leachates collected from Fe(II) treated zone was varied between 8.1 to 8.3. High concentrations of Ca, S, and Na observed in the effluent reflected the high salt content of the profile originating from the tannery waste.

Unlike the low concentration of Cr(VI) recorded in the pore water from the treated zone, the concentrations of Cr(VI) from the 10 cm depth were high and did not increase with time. Speciation of Cr in the the leachate collected from 10 cm port showed that all the Cr leached from this zone was probably in the Cr(VI) form and no Cr(III) was detected in the leachate. Consistent with the observations in the effluent from the 5 cm port, effluent from 10 cm also showed considerable release of soluble cations and sulphate from the intact core. No soluble Fe was detected in leachate from 5 or 10 cm which indicated that all the incorporated Fe(II) salt was either oxidized by Cr(VI) or lost through adsorption and oxidation by O_2. The high soil pH also favoured adsorption in preference to migration of Fe to the subsurface layers.

The effluent collected from the 10-30 cm zone showed higher Cr concentrations compared to the concentrations of Cr released at 5 cm and was even greater than that observed from the untreated zone at 10 cm. Speciation studies showed that Cr in the effluent was predominantly Cr(VI). This suggests that Fe(II) incorporated ~~on~~ into the surface layer was not effective in reducing soluble Cr(VI) in the 10 - 30 cm layer.

The reasons for the lack of complete reduction and reappearance of Cr(VI) may be due to the presence of a large pool of labile Cr(VI) and the limiting amount of added Fe(II). This limitation in Fe(II) may be due to (a) leaching of Fe(II) to subsurface soils (but no Fe was detected in the ~~leachates~~ pore waters from subsurface ports and so this seems unlikely) or (b) the loss of Fe(II) to ion exchange processes and oxidation to Fe(III)(OH).

In Chapter 9 the main focus was to develop an innovative technique for removing Cr(VI) from wastewater and to minimize Cr contamination of land from wastewater disposals. Most current water treatments for Cr(VI) consists of a two-stage process: Step 1, the reduction of Cr(VI) to Cr(III) and, Step II, the precipitation of the Cr(III). However, here the direct removal Cr(VI) from water was attempted using a lanthanum salt. This was based on the report of Tokunaga et al., (1999) who demonstrated that lanthanum (La^{3+}) salts could be used to precipitate and remove arsenite, As(III) and arsenate, As(V) from waters.

The lanthanum chloride salt was found to be effective in removing Cr(VI) from solutions as a $La_2(CrO_4)_3.7H_2O$ precipitate. The formation of $La_2(CrO_4)_3.7H_2O$ was supported by the X-ray diffraction (XRD) patterns of the purified precipitates (Leppa-Aho and Valkonen, 1994). At high initial concentrations of Cr(VI) (0.1 M), Cr(VI) removal was 98% at 1:1 mole ratio and 93% for 1:2 mole ratio of La^{3+} to Cr(VI).

However, more La^{3+} was required to remove Cr(VI) at low initial concentration of Cr(VI) (1 mM). The ratio of 5:1 of La^{3+} and Cr(VI) effectively removed 99% of Cr(VI) from solutions. The optimum pH for Cr(VI) removal by La^{3+} was 6.3 for high initial concentrations of Cr(VI) and a pH range of 7.5 – 8.5 was effective in removing Cr(VI) from low initial concentrations of Cr(VI). In general, a pH range of 6 – 8.5 was found to be ideal for complete removal of Cr(VI) from solutions by La^{3+}.

Future Research

Future research needs to be directed towards the sustained availability of aqueous Fe(II) for a complete stabilization of Cr(VI) in Cr contaminated soils. Soil pH is a key factor and lowering the soil pH by only 1 unit in tannery contaminated soils may assist in lowering the doses of Fe(II) required due to an increase in sustained availability of aqueous Fe(II) for the successful reduction of Cr(VI) in these soils.

The work on Cr(VI) precipitation by La^{3+} needs to be extended to include Cr(VI) contaminated groundwater and industrial waste waters where a mixture of other dissolved salts may interfere with Cr(VI) precipitation.

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Journal of Chromatography A, 927 (2001) 219–227

JOURNAL OF
CHROMATOGRAPHY A

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Separation of chromium (III) and chromium (VI) by capillary electrophoresis using 2,6-pyridinedicarboxylic acid as a pre-column complexation agent

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Received 18 April 2001; received in revised form 27 June 2001; accepted 10 July 2001

Abstract

A simple method was developed for the simultaneous determination of Cr(III) and Cr(VI) by capillary zone electrophoresis (CZE), where Cr(III) was chelated with ligands to form anionic complexes. Nitrilotriacetic acid, *N*-2-hydroxyethylenediaminetriacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and 2,6-pyridinedicarboxylic acid (PDCA) were investigated as Cr(III) complexing ligands. Of all the ligands studied, 2,6-PDCA with Cr(III) gave the largest UV response and high selectivity for Cr(III). In addition, the condition for pre-column derivatization, including pH, concentration ratio [Cr(III)/2,6-PDCA] and the stability of Cr(III) complexes were also examined. The separation of anionic forms of Cr(III) and Cr(VI) was achieved using co-CZE with UV detection at 185 nm. The electrolyte contained 30 m*M* phosphate, 0.5 m*M* tetradecyltrimethylammonium bromide, 0.1 m*M* 2,6-PDCA and 15% (v/v) acetonitrile at pH 6.4. The detection limits were 2 μ*M* for Cr(III) and 3 μ*M* for Cr(VI) and linear plots were obtained in a concentration range of 5–200 μ*M*. The utility of the method was demonstrated for the determination of Cr(III) and Cr(VI) in contaminated soils. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Complexation; Soil; Environmental analysis; Chromium; Metal cations; Pyridinedicarboxylic acid

1. Introduction

The speciation of metal with different oxidation states exhibits widely different behaviours in terms of potential toxic effects on environmental and biological system. For chromium, the two most environmental important oxidation states are Cr(VI) and Cr(III). Cr(VI) can be readily reduced to Cr(III) in the biosphere, and both can be taken up by humans and other ecological receptors [1]. Recently, much of the interest arises from the growing need to identify the chromium speciation responsible for toxic effects on environmental and biological systems [2], e.g., Cr(VI) is highly toxic even in a small concentration, however Cr(III) can be considered as an essential element for human beings in a proper concentration range, and it can be toxic only in very high concentrations. There are many methods used for the determination of chromium speciation. Methods mainly include flow injection analysis (FIA) or liquid chromatography (LC) coupled with different detection techniques [3]. FIA with either off-line or on-line preconcentration is frequently used where the species are detected using electrochemical detection

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PII: S0021-9673(01)01116-5

(ED) [4], spectrophotomety (UV–Vis) [5,6], chemiluminescence (CL), fluorimetry (FL) [7–9], or atomic absorption spectrometry (AAS) [10–13]. During LC [14], chromium species can be separated by reversed-phase chromatography after the formation of neutral chelates by the addition of a complexing agent to the mobile phase [15,16], ion-paring [17–19] or ion chromatography [20,21]. It may also be coupled with atomic emission spectrometry (AES), or inductively coupled plasma mass spectrometry (ICP-MS) [15–21]. These methods are all useful techniques and offer high detection sensitivity for chromium in environmental samples. However, they still do not satisfy all requirements for routine analysis because of their complicated process design and the need for expensive instruments in the case of AAS and ICP-MS.

Capillary electrophoresis (CE) is an attractive approach for the separation of metal species [22] due to its high efficiency and separation speed. One of the problems using CE for the separation of cations has a similar mobility, resulting in poor resolution. However, complexation of cations with a ligand to form anionic complexes can be used to modify the mobility of the cation as each cation will complex with the ligand to a different degree determined by the complexes stability [23,24]. In principle, two approaches are used in the CE separation of metals. One is on-line complexation, where a soluble ligand is added to the running electrolyte and weak complexes are rapidly formed. Indirect UV detection is usually employed and carboxylic acids are usually used as the weak ligands [23,24]. Another approach is pre-column complexation, where an excess of strong ligand is added to the sample to form complexes prior to CE analysis [25]. This method allows for direct UV detection of the metal ions after chelating with suitable UV absorbing ligands. Compared to indirect UV detection, the latter approach is more preferable due to increase selectivity and sensitivity [25], and has been used successfully for the analysis of real samples [26–28].

Pre-column complexation CE methods have recently been reported for the separation of Cr(III) and Cr(VI) [25]. Normally Cr(III) and Cr(VI) cannot be separated by CE. The reason is that their charge is opposite and charge values are different. However, when Cr(III) is complexed with a suitable ligand, to form an anionic complex, it is possible to simultaneously determinate oxidation states in one run. Aminopolycarboxylic acids, including ethylenediaminetetraacetic acid (EDTA), 1,2-cyclohexanediaminetetraacetic acid (CDTA), diethylenetriaminepentaacetic acid (DTPA), have been used as ligands to convert Cr(III) into negatively charged complexes and successfully used to the determination of chromium in real samples [29–34]. Oleski et al. described that the determination of Cr(II) and Cr(II) by CE–ICP-MS using 8-hydroxyquinone-5-sulfonic acid as a complexing reagent [33], and Mei et al. reported that the use of CE–ICP-AES for the determination of these species [34]. Recently, Himeno et al. [35] have reported the use of Mo(VI) reacted with Cr(III) to form water-soluble $[CrMo_6O_{24}H]^{3-}$, followed by CE separation with direct UV detection. Previously, 2,6-pyridinedicarboxylic acid (2,6-PDCA) had been used as the electrolyte for CE separation of metals such as Ni(II), Cu(II) and Fe(II) and organic anions [36,37], and mobile phase in ion chromatography for indirect UV detection of inorganic anions, cations, and carboxylic acids in ion chromatography [38,39]. These results suggested that 2,6-PDCA offered a high selectivity and UV responsive ligand for metal ions. In this paper, we report the separation of Cr(III) and Cr(VI) by CE with direct UV detection in a single run based on Cr(III) complexation with 2,6-PDCA. In order to evaluate the proposed method, 2,6-PDCA was also compared to other ligands commonly used in CE analysis. The proposed method was applied to the determination of aqueous chromium speciation in a long-term tannery contaminated soil.

2. Experimental

2.1. Chemicals

All reagents (analytical grade) were obtained from Sigma–Aldrich (Sydney, Australia) and dissolved in Milli-Q water without further purification. Standard solutions of the $K_2Cr_2O_7$ and $CrCl_3 \cdot 6H_2O$ were prepared daily from a 10 m*M* stock solution in Milli-Q water and diluted to the required concentrations before use. Electrolyte required for CE was prepared by dissolution of an appropriate amount of NaH_2PO_4 in Milli-Q water, where contained appropriate amounts of tetradecyltrimethylammonium bromide (TTAB) and organic solvent. All electrolytes were filtered through a Millipore 0.45-μm membrane filter and degassed in an ultrasonic bath prior to use. Electrolyte pH was adjusted with 0.1 *M* NaOH or 0.1 *M* H_3PO_4 solution.

2.2. Sample preparation

An excess of ligand, 4 m*M* ligand (1.0 ml), was added to a tube containing 1 m*M* $CrCl_3{\cdot}6H_2O$ (0.5 ml) and heated on a water bath for 5 min at 80°C. Heating is required because of Cr(III) kinetics inert. A 0.5-ml volume of $CrCl_3{\cdot}6H_2O$ (1 m*M*) solution was transferred to a test tube and excess 1.0 ml ligand (4 m*M*) added [30]. After cooling to room temperature, the mixture was subjected to CE analysis. Soil solution was obtained by exchanging the contaminated soil with water in a 1:5 ratio (soil: deionised) for 2 h in an end over end shaker, centrifuging at 3200 *g* for 15 min and filtering through 0.45-μm Schleicher and Schuell syringe filters. Total Cr and soluble Cr(VI) in the soil solution was analysed in the same day.

2.3. Instrumentation

All CE experiments were performed using a Quanta 4000 instrument (Waters, Milford, MA, USA). The system was controlled by Millennium (Waters) software. Separation was carried out on fused-silica capillaries of 80 cm (effective length 75.5 cm)×50 μm I.D. The UV detector was set at 185 or 214 nm. Total Cr was determined using AAS (GBC, Model 906, Australia). Cr(VI) was analysed by ion chromatography using standard method 7199 [40]

2.4. Electrophoretic procedures

Prior to use, a capillary was pretreated with the following cycles: 0.1 *M* NaOH for 20 min, 0.01 *M* NaOH for 20 min, deionised water for 30 min and 30 m*M* phosphate buffer for 30 min. The capillary was pre-conditioned with phosphate buffer for 2 min for each run. Samples were injected in the hydrostatic mode for 30 s. The capillary was held at 25°C, and the applied constant voltage was −20 kV. Identification of each of the solutes was based on the migration time and was verified by spiking samples with known standards. 0.05% (v/v) benzyl alcohol was used as a neutral marker for the determination of the electrophoretic mobility. The electroosmotic mobility and the electrophoretic mobility of the solute and marker were calculated using equations described previously.

3. Results and discussion

3.1. Choice of complexing ligand for Cr(III)

In order to achieve high UV response and selectivity, complexing ligands should satisfy several requirements including (1) the ligand should only form a single distinct complexing with Cr(III) under derivatization conditions; (2) the complex remains stable during electrophoresis, and (3) the complex has large UV absorptivity [25,41,42]. In this work, EDTA, *N*-2-hydroxyethylethylenediaminetriacetic acid (HEDTA), DTPA, nitrolotriacetic acid (NTA) and 2,6-PDCA were used as ligands for chelation with Cr(III). The complexes formed were separated using an electrolyte containing 30 m*M* phosphate, 0.5 m*M* TTAB at pH 6.0 as shown in Fig. 1a–e. For all five ligands, the Cr(III) complexes were detected longer with excess free ligand. The free ligand peak appeared before the Cr(III) anionic complex peaks because their charge/mass ratio was greater than that of the Cr(III) complexes. However, two or more peaks and a small UV response were observed using EDTA, HEDTA and DTPA. This can be attributed to the formation of different Cr(III) anionic complexes under the derivation conditions [22]. In contrast, only one complex peak was observed using either 2,6-PDCA or NTA as a complexing ligand. However, a larger UV response for the Cr(III) complex was obtained using 2,6-PDCA due to the complex absorptivity (43 680 M^{-1} cm^{-1}, 192 nm) [36]. However, in this study, there was less UV response for all five ligand complexes at 214 nm. This is not unexpected, since the carboxylate group of the ligand has stronger absorbency below 210 mn [29,30,32]. For example, Cr(III) chelated with 2,6-PDCA at 185

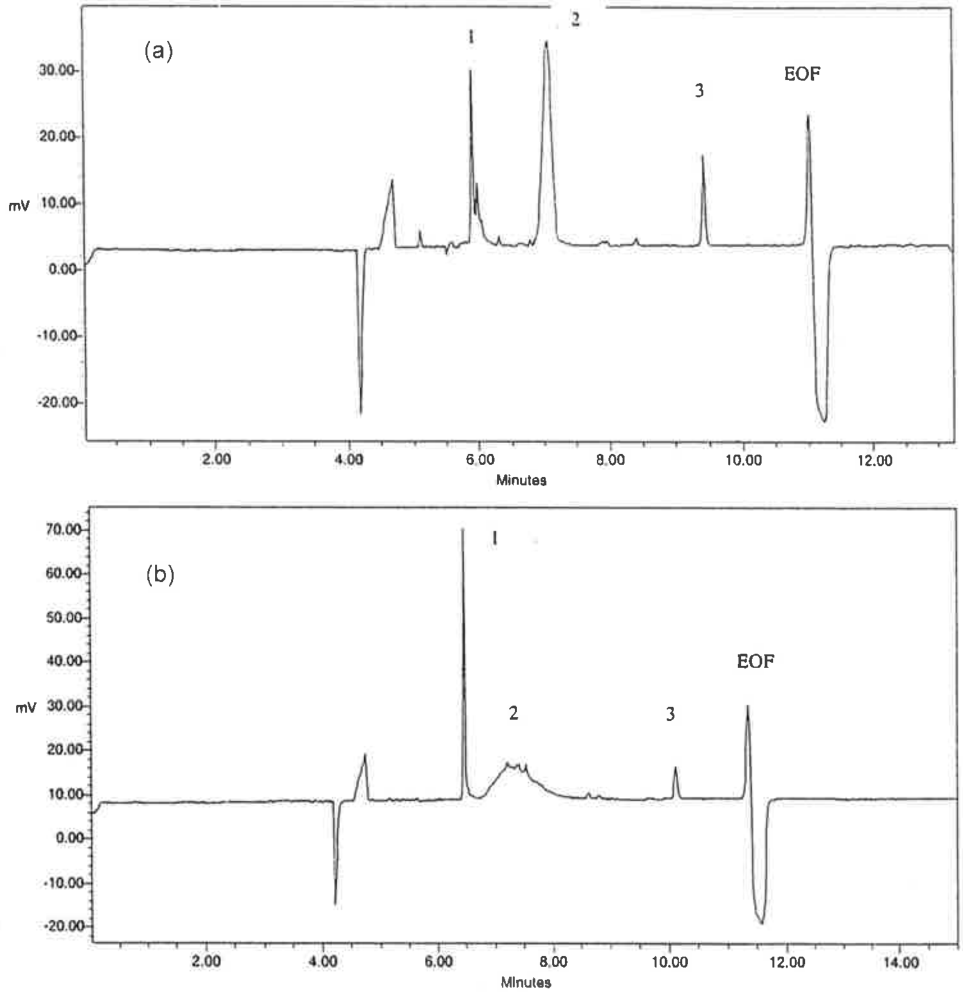

Fig. 1. Electropherograms of Cr(III) complexed with various ligands. (a) EDTA, (b) HEDTA, (c) DTPA, (d) NTA, (e) 2,6-PDCA. 1, Free ligand; 2, Cr(III) complex (I); 3, Cr(III) complex (II). 0.25 m*M* for Cr(III). Conditions: capillary, fused-silica capillary 80 cm (effective length 75.5 cm)×50 μm; electrolyte, 25 m*M* sodium phosphate, 0.25 m*M* TTAB, 15% (v/v) acetonitrile at pH 6.40; applied potential, −20 kV; hydrostatic injection, 30 s, UV detection at 185 nm. Capillary temperature, 25°C.

nm had a peak area six-times greater than that obtained at 214 nm. The selectivity of the ligand for common metal ions [Ca(II), Mg(II), Mn(II), Zn(II), Co(II), Cd(II), Ni(II), Cu(II), Pb(II), Fe(III)] was also tested. This indicated that EDTA, HEDTA and DTPA chelated with most of the tested metal ions, while NTA and 2,6-PDCA showed a higher selectivity for Cr(III). Although 2,6-PDCA complexes with Ni(II), Cu(II) and Pb(II) forming $(M[L]_2)^{2-}$ [43], these complexes have significantly different mobilities to $[Cr(L)_2]^{1-}$ due to the lower charge and therefore does not interfere with the determination of Cr(III). Thus, 2,6-PDCA was the more suitable ligand for Cr(III) determination because it satisfied above the requirements most readily.

3.2. Pre-column derivatization conditions

Work on 2,6-PDCA as an eluent in ion chromatography [44,45] has shown that eluent pH and ligand concentration play important roles in the formation of anionic complexes. Similarly, the conversion of Cr(III) to an anionic Cr(III) complex is highly

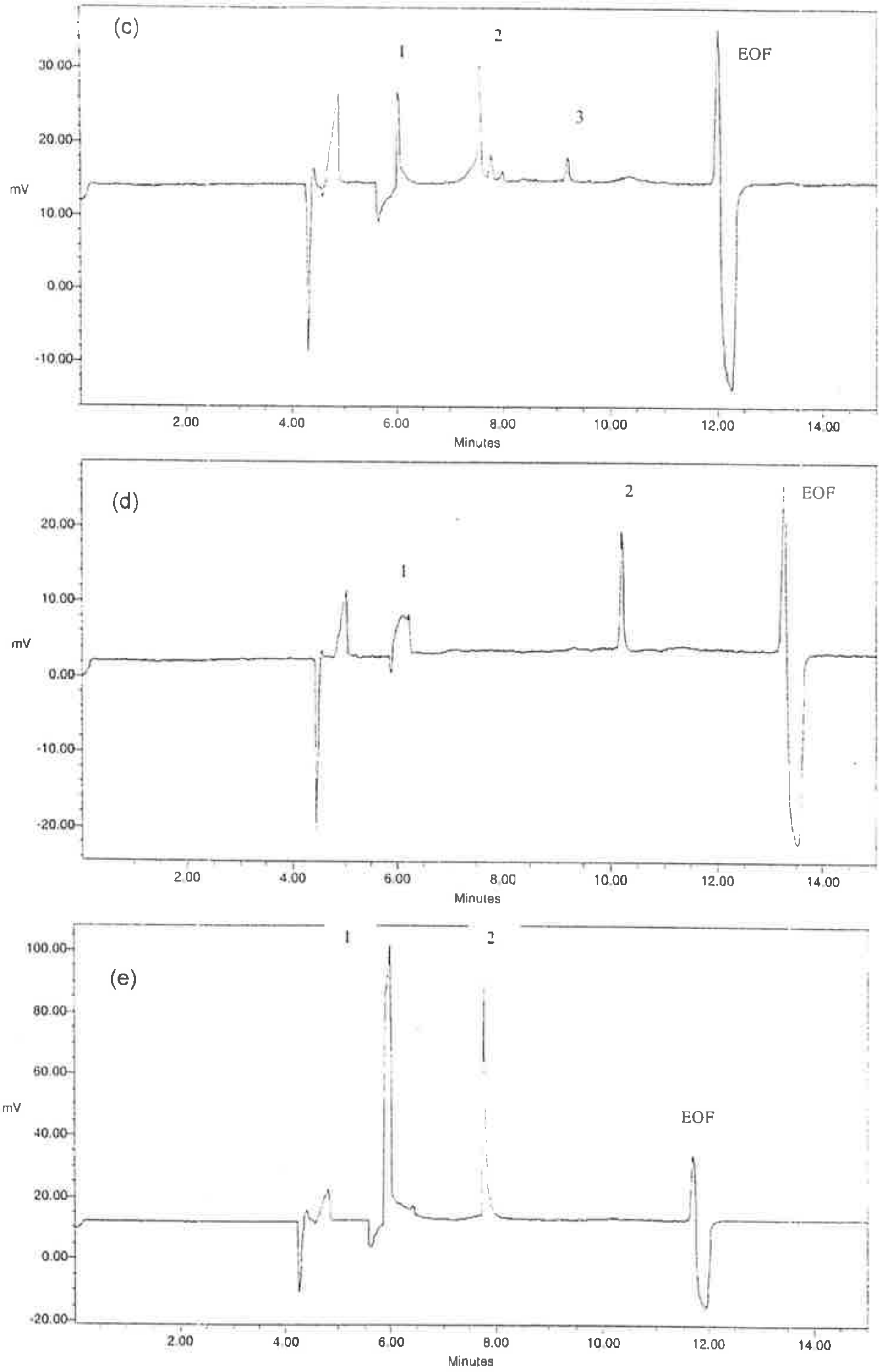

Fig. 1. (*continued*)

dependent upon on pH and the concentration as shown by the following equations [43]:

$$\mathrm{Cr^{3+} + 2PDCA^{2-} = [Cr(PDCA)_2]^-} \quad (1)$$

$$\mathrm{H_2PDCA = 2PDCA^{2-} + 2H^+} \quad (2)$$

$$\mathrm{Cr(OH)_3 = Cr^{3+} + 3OH^-} \quad (3)$$

Since the pK_a values for 2,6-PDCA are pK_{a1} 2.16, and pK_{a2} 6.92, the pH was tested in the range 2.5–7.5. The formation of $[\mathrm{Cr(PDCA)_2}]^-$ was determined by co-CZE at 185 nm. Fig. 2 shows that the formation of $[\mathrm{Cr(PDCA)_2}]^-$ significantly depends on the solution pH. Peak area was increased as the pH was increased from 2.5 to 3.5. This can be attributed to an increase in the concentration of $\mathrm{PDCA^{2-}}$, leading to formation of $[\mathrm{Cr(PDCA)_2}]^-$ via Eq. (1). In contrast, peak area decreased when solution increased above 4.0. A higher solution pH leads to the hydrolysis of the Cr(III) and to the formation of the precipitate described via Eq. (3). Therefore, the optimum solution pH of 3.5 was used in all subsequent experiments.

From Eq. (1), it can be seen that concentration ratio (Cr(III)/2,6-PDCA) during derivatization affected the formation of $[\mathrm{Cr(PDCA)_2}]^-$. The affect of the concentration ratio is shown in Fig. 3. In general, peak area increased as the concentration ratio increased, peak area increased linearly up to a concentration ratio of 4. However, when ratio was above 6, the peak area was almost constant. At all concentration ratio only a single complex peak was observed. Similar results have been observed previously [38,39]. A higher concentration ratio favours the forward chelating reaction because of the increasing of the concentration of 2,6-PDCA. Therefore, the best concentration ratio for obtaining maximum sensitivity was 6 [Cr(III)/2,6-PCDA].

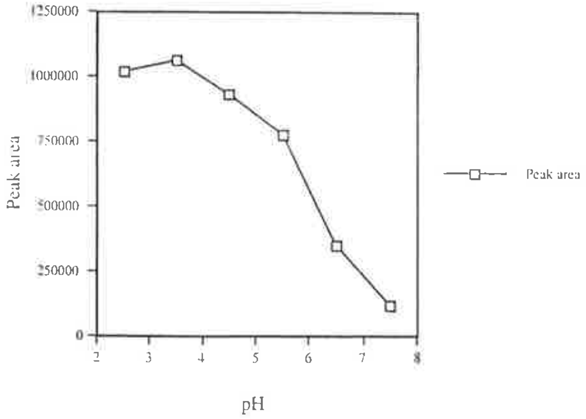

Fig. 2. Effect of pH on the chelating reaction between Cr(III) and 2,6-PDCA. 2,6-PDCA: 1.0 m*M*; Cr(III): 0.25 m*M*. Separation conditions as in Fig. 1.

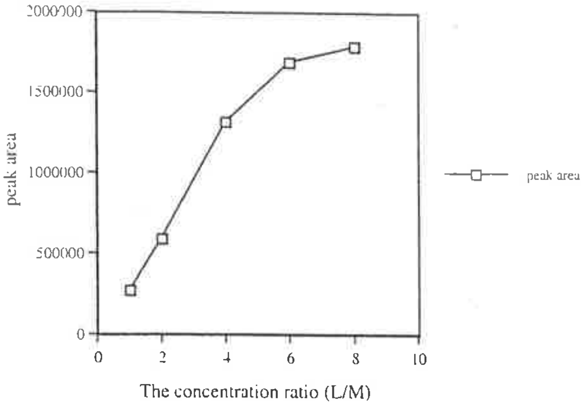

Fig. 3. Effect of the concentration ratio (*L*/*M*) on the derivatization. Solution pH: 3.5. Conditions as in Fig. 1.

The stability of $[\mathrm{Cr(PDCA)_2}]^-$ was determined by repeated injections of solution derivatized at the concentration ratio of 6 at pH 3.5. The derivatization solution was then stored at room temperature and re-analysed every day. The solution exhibited well a stability for up to 5 days (the response obtained from the sample at fifth day is 96.5% of that at on the first day) at room temperature with no degradation being detected by CE. This indicates 2,6-PDCA was suitable for pre-column derivatization of Cr(III) with high selectivity.

3.3. Simultaneous separation of Cr(III) and Cr(VI)

As shown in Eqs. (1)–(3), there is a dynamic equilibrium between Cr(III), 2,6-PCDA and $[\mathrm{Cr(PDCA)_2}]^-$. The equilibrium shifts during electrophoresis due to the dissociation of $[\mathrm{Cr(PDCA)_2}]^-$. This problem can be overcome by the addition of small amounts of ligand to the running electrolyte [25,29–32]. In addition, the selectivity for the separation of metal anionic complexes can be controlled by the addition of organic solvent [25]. Thus, an

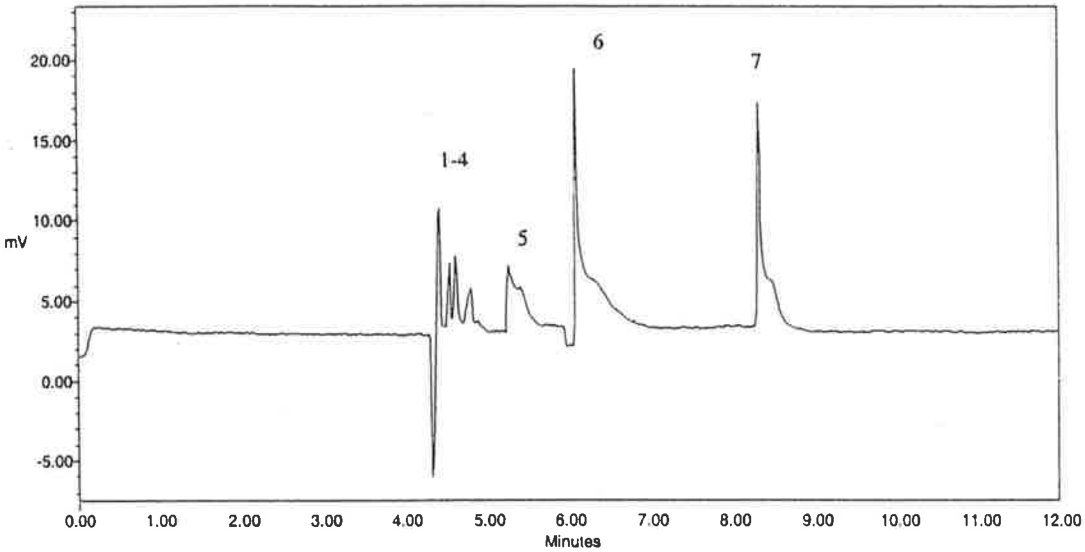

Fig. 4. Separation of Cr(III) and Cr(VI) under optimum CE conditions. 1, Cl (0.25 m*M*); 2, NO_2 (0.25 m*M*); 3, NO_3 (0.25 m*M*); 4, SO_4^{2-} (0.25 m*M*); 5, Cr(VI) (0.1 m*M*); 6, 2,6-PCD (0.25 m*M*); 7, Cr(III) complex (0.05 m*M*). Conditions: electrolyte: 30 m*M* sodium phosphate + 0.5 m*M* TTAB + 0.1 m*M* 2,6-PDCA + 15.0% (v/v) acetonitrile at pH 6.40. Other conditions as in Fig. 1.

electrolyte, containing 30 m*M* phosphate, 0.5 m*M* TTAB, 0.1 m*M* 2,6-PDCA, and 15% acetonitrile at pH 6.40, was used as the running buffer for the separation of CrO_4^{2-} and $[Cr(PDCA)_2]^-$, and detected by direct UV at 185 nm. CrO_4^{2-} and $[Cr(PDCA)_2]^-$ were generally well separated and well defined peaks. Excess of 2,6-PDCA was also detected, appearing prior to $[Cr(PDCA)_2]^-$ due to the large charge and small size. Some inorganic anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) commonly present in soils were added to the mixture of CrO_4^{2-} and $[Cr(PDCA)_2]^-$ to determine whether they interfered with CrO_4^{2-} and $[Cr(PDCA)_2]^-$. Fig. 4 clearly demonstrates that Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, CrO_4^{2-} and $[Cr(PDCA)_2]^-$ were all well resolved. The migration order was Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, CrO_4^{2-} and $[Cr(PDCA)_2]^-$. The migration order reflects differences in both charge and size of the solutes. For example, CrO_4^{2-} is double negatively charged and migrates faster than $[Cr(PDCA)_2]^-$ which is only single negatively charged.

Calibration plots were obtained by plotting peak area versus concentration. The relationship was linear in the concentration range 5–200 μ*M*. Correlation coefficients (r^2) were in the range 0.9992–0.9999. The detection limits ($S/N=3$) were 2–3 μ*M* and the reproducibility of the migration time (relative standard derivation, $n=5$) from injecting a 100 μ*M* standard mixture was 0.7–2.4%. Analytical characteristics of the test solutes using the proposed method are listed in Table 1.

The proposed method was used to determine Cr(III) and Cr(VI) in extracts of the contaminated soils. A typical electropherogram is presented in Fig.

Table 1
The characteristics for chromium species by the proposed method

Species regression line	Coefficient	Detection limit (μ*M*)	Reproducibility ($n=5$, %)
Cr(III) $y=10\cdot10^5x-4.5\cdot10^3$	0.999	3	2.0
Cr(VI) $y=5.63\cdot10^5x-1.5\cdot10^3$	0.998	2	2.4

Conditions as in Fig. 4. Detection limit – signal/noise = 3.

5a. The contaminated soil contained only Cr(VI) in detectable concentrations. The peak assessment was verified by spiking the solution with a known concentration of Cr(VI) as shown in Fig. 5b. To confirm the proposed method for the determination of Cr(III), a known concentration of Cr(III) was also added to the soil. The determined concentrations are listed in Table 2, together with the concentration

Table 2
The concentration of Cr(III) and Cr(VI) in contaminated samples determined by the CZE and UV methods

Species	CE (mg/l)	UV (mg/l)	Spiked (mg/l)	Found by CZE (mg/l)	Recovery ($n=3$, %)
Cr(III)	–	–	2	1.96	98.0±3.8
Cr(VI)	0.483	0.486	2	2.48	99.7±2.9

Conditions as in Fig. 4.

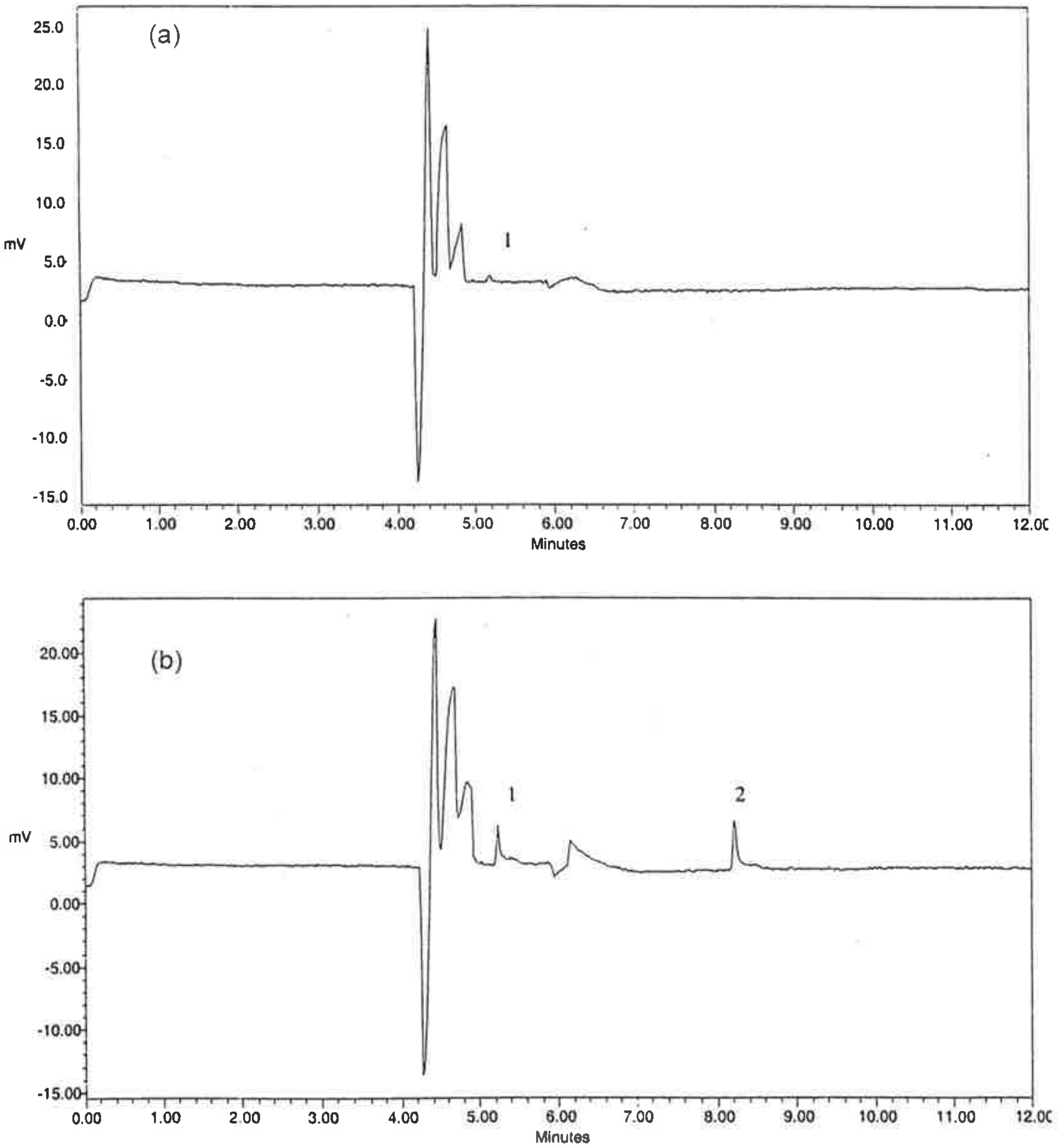

Fig. 5. Contaminated soil extracts analysed by the proposed method. (a) Soil extracts, (b) soil extract spiked known Cr(VI) and Cr(III). 1, Cr(VI); 2, Cr(III). Conditions as in Fig. 4.

determined with spectrophotometry. The results obtained using CE method showed good agreement with results obtained using spectrophotometry.

4. Conclusion

The results of this work demonstrate that 2,6-PDCA can be used as a derivatizing agent for Cr(III) and is therefore a useful ligand for the determining chromium speciation when using CE with direct UV detection. The derivatization conditions, such as solution pH and the concentration ratio (*M*/*L*) are both important for the formation of a single stable $[Cr(PDCA)_2]^-$ complex. The proposed method offers high separation efficiency and short analysis time in comparison with conventional spectrophotometric methods. However, the detection limit still does not as yet satisfy that required for real samples. Preconcentration of Cr(III) and Cr(VI) based on solid-phase extraction is being developed to address this problem.

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